Rinse Optimization
For Reduction of Point-of-Use Ultrapure Water Consumption
In High Technology Manufacturing

Prepared by

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1. Executive Summary

Manufacturing of high technology products like semiconductors, data storage media and printed wiring board continues to be an essential part of the South Bay economy. The cleaning and rinsing processes in the manufacturing of these devices and other high tech products (like flat panel display) consumes significant amounts of ultrapure water (UPW). This poses challenges to both the costs of manufacturing and impact on local environment. An obvious solution and the approach taken here is to reduce point-of-use water consumption. In this way, manufacturing costs can be reduced and significant environmental benefits can be realized.

Most of the UPW used in high tech manufacturing is for rinsing between chemical steps in the manufacturing process flow. The objective here is to reduce UPW consumption, by optimizing rinse processes. There are significant benefits to developing optimized processes which include reduced water consumption, shorter process times, higher tool utilization and higher throughputs - all leading to lower manufacturing costs and environmental benefits. This report includes work on rinse optimization performed at the South Bay high tech manufacturers, Hadco Santa Clara (Printed Wiring Board), MMC Technology (Disk Drive), Intel Corporation and Agilent Technologies (Semiconductors). These companies were selected because they discharge more than 100,000 gallons of wastewater per day. A site assessment was performed at each of these companies and, with the exception of Intel, a summary is included in this report. Intel had already received technology transfer of rinse optimization through International Sematech, so project resources were used at the other three sites.

Implementation of the recommendations made in the site visit reports can lead to reduction in rinse process times of 25% - 80% and water savings of 25% - 80%. Total UPW savings based on the findings presented here for the three companies assessed is 42.6 million gallons per year. Assuming UPW costs $0.1/gallons for city feed, processing and sewer cost, direct annual cost savings would be $4.26 million. Greater savings in manufacturing costs can be realized through cost avoidance of water processing and waste treatment plants and reduction in the number of production tools.

2. **Project Background** (contributed by Chris Elias)

In 1997, the City of San Jose, through its Environmental Services Department began a collaboration with the private sector to seek ways to reduce the amount of wastewater being discharged to the San Jose/Santa Clara Water Pollution Control Plant (Plant). This collaboration is an important part of a larger effort to continue to protect and restore the salt marsh habitat of two endangered species by reducing the amount of freshwater flows from the Plant to to the South Bay.

In 1999 the Silicon Valley Manufacturing Group (SVMG) and the Silicon Valley Pollution Prevention Center were approved for a joint grant from the City of San Jose's Watershed Grant program to promote the technology transfer of ultrapure water rinse optimization within the semiconductor industry to other types of electronic manufacturers. The SVMG contacted its member companies whose facilities were listed as Tier 1 dischargers (> 100,000 gpd), to solicit volunteers for participation in this project. A key element to the success of this project was to find a consultant who had the respect of the semiconductor industry, the experience and the technical expertise in high tech water quality issues and manufacturing processes necessary to assess the applicability of this technology transfer. After an extensive search for a technically competent consultant, the Manufacturing Group, in partnership with the Silicon Valley Pollution Prevention Center, selected Dr. Ronald Chiarello of Stanford University. Dr. Chiarello's work on reductions of ultrapure water in high technology manufacturing has lead to significant cost savings, enhanced productivity and environmental benefit for factories in the US, Europe and Asia. Under the watershed grant agreement from the City, Dr. Chiarello evaluated and discussed specific water reduction projects with some of the largest dischargers in the high-tech industry, including HADCO of Santa Clara, MMC Technology, Intel, and Agilent Technologies.

3. Rinse Optimization Methodology

The methodology for optimizing rinse processes was developed and tested in semiconductor manufacturing. It has also been applied to disk and head manufacturing in the data storage industry. The result presented in this report mark the first application of this methodology to printed wiring board manufacturing.

Any optimized rinse strategy must provide equal or better performance compared to current best practices. The basis for evaluating and implementing optimized rinse processes is data acquired in the fab under production conditions. This includes

1. Wet tool water use survey to determine the overall efficiency of water use and water management. Water flow rates for both process and idle flow, fluid dynamics, evaluation of chemical and gas additives to rinse water, use of megasonic energy, water temperature, transfer speeds from chemical baths to rinse tanks, etc.
2. Detailed conductivity, pH and ICP-mass spectrometry measurements to determine the quantity and type of contaminants in rinse water as a function of rinse time and as a function of UPW use.
3. Wafer, disc or wiring board surface measurements including light point defect (LPD), surface metal and organic contamination, oxide etch uniformity, pitting, etc.
4. Device electrical characteristics to determine what effect, if any optimized rinse processes have on device yield (optional).

Wet tool water use surveys include measuring UPW flow rates as a function of tool utilization and often lead to large UPW savings. UPW idle flow rates are used when tools are not processing wafers to reduce bacteria formation in rinse tanks. Studies performed by semiconductor manufacturers and tool suppliers indicate that idle flow rates of 0.5 to 1 liter/min are sufficient. Reducing idle UPW flow rates in a 200-mm semiconductor fab by only 1 liter/min would save more than 6 million liters of UPW per year. This type of optimization does not require re-qualification of the process flow making implementation more convenient.

Rinse process optimization requires information on the composition of contaminants in rinse waters and any effects that the new rinse strategy have on product surface quality. Specific measurements for rinse waters include conductivity (or resistivity), pH, liquid particle counts, bacteria and ion coupled plasma (ICP) mass spectroscopy to determine quantities and types of contaminants. This information is highly useful for recycling/reclaim to determine contaminant concentrations in waste streams as a function of UPW use. This data determines how rinse water is segregated and treated for recycle and reclaim.

Product surface analysis correlates changes in rinse water contamination levels with product surface quality and cleanliness. Measurements include total x-ray fluorescence (TXRF) for surface metal concentrations, light point defect (LPD) for particles, ellipsometry for oxide etch uniformity, and mass spectroscopy for organic contamination.

4. Hadco Santa Clara Report 1

Site Visit Report for Water Use Reduction

Hadco Corporation, Santa Clara, CA

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Silicon Valley Manufacturing Group supported this work.

September 2, 1999

Executive Summary

The objective of this program is to realize gains in performance improvements, cost savings and environmental concerns by reducing point-of-use water consumption. The recommendations made in this report can allow for increased capacity at the Santa Clara site without increasing water consumption or the footprint of the wet process area electroplating lines.

This report represents observations and recommendations determined from the initial site visit to the Outer-layer Wet Process Area at Hadco's Santa Clara site. Both the automated and manual wet process-electroplating lines were observed during full operation. Specific observations for water use reduction include:

1. Implementation of idle flow rates when rinse tanks are not in processing product. Estimated water reduction is 40,000 gallons per day.
2. Reduce rinse tank volumes and process flow rates from 6 gpm to 2 gpm in the automated lines. This will improve rinse effectiveness, reduce electroplating process line footprint and reduce water consumption by 43,200 gallons/day.
3. Reclaimed footprint can be used to increase the Cu electroplating area, thereby increasing throughput and capacity without increasing tool footprint
4. Determine acceptable water quality in rinse tanks and implement in-line recycling and reclaim. Calculations by Don Hoppe show 42% water reduction is possible.

These recommendations represent cost-effective methods for increasing capacity while decreasing water consumption and process line footprints.

2. Observations and Recommendations

Fully Automated Electroplating Line

The process flow for the Electroplating Line includes the following process steps:

1. Surfactant-based Cleaner (5 minutes).
2. Rinse 1, includes sprayers to rinse flight bars (2.5 minutes).
3. Rinse 2, (2.5 minutes).
4. Micro-etch, sodium persulfate.
5. Rinse 3, counter flow rinse.
6. Sulfuric Acid Dip (10%).
7. Cu-plating (1.5 hours).
8. Rinse 4, drag out static rinse.
9. Fluoboric Acid.
10. Lead-Tin Alloy (solder).
11. Rinse 5, drag out static rinse.
12. Rinse 6, counter-flow rinse.
13. Rinse 6, hot water rinse.

Rinse Tank 1 (process step 2) has a volume of 420 gallons and a water up-flow rate of 6 gpm. The overhead spray showers are used to rinse chemical carryover from the surfactant-based cleaning bath. Water is injected into the rinse tank using a sparge pipe, with flow directed towards the bottom of the tank at a 45° angle. This flow geometry is used to create a continuously stirred reactor (CSTR) scenario in rinse tank 1. The CSTR scenario should provide ideal mixing of water introduced into the tank with chemical carryover from the surfaces of the circuit boards and their holders. Additionally, water flows out of one side of the rinse tank. In this geometry, the effective water flow velocity in parts of the rinse tank is small. In these areas of the rinse tank, contamination must diffuse to the drain, which is an ineffective method for removing chemical residue from rinse tanks. For example, a typical acid molecule has a diffusion rate of approximately 1µm/s. At this rate it may take several hours for contamination to travel to the drain. The solution is to improve the fluid dynamics of the rinse tank by incorporating four-sided drain geometry, reducing the size of the rinse tank and placing a sparger plate at the bottom of the tank where water is introduced.

The CSTR scenario can be contrasted with the plug flow reactor scenario. In this case, as water is introduced into the rinse tank, chemical residue is not mixed with water introduced into the bottom of the rinse tank. Instead, chemical carryover is pushed out of the top of the rinse tank without mixing. Plug flow is usually accomplished using a sparge plate at the bottom of the rinse tank and using the water up-flow rate to control laminar flow. Plug flow is typically desirable for post-cleaning chemical rinses and CSTR is desirable for post-etch rinses. This is because the plug flow rinse is more efficient for removing chemical carryover. Here the metrics for determining efficiency are the rinse time and water consumption needed to remove 100% of chemical carryover from the rinse tank. In addition, metrics for determining product surface quality is needed. An example is removal of micro gas bubbles from the connecting holes in the Printed Wiring Boards (PWBs).

In the Semiconductor Industry, the CSTR rinse model is typically desired for rinsing following etching steps and the plug-flow reactor model is often applied to rinsing following cleaning steps. The plug-flow method may provide a more efficient rinse, the CSTR scenario will provide better etch uniformity by homogeneously mixing etch chemical carryover with water during the rinse process. There fore, during the rinse process the surface of the material is uniformly exposed to increasingly dilute quantities of the etch chemical as a function of rinse time. Ultimately, the surface is exposed to ultrapure water.

One of the key efficiency metrics of any rinse process is dilution of chemical carryover. This is accomplished by turning over rinse tank volume with incoming water. For rinse tank 1, at 420 gallons and 6 gpm, the rinse tank volume is turned over once every 70 minutes. For a rinse time of 2.5 minutes, only one out of every 28 lots (one lot = 16 PWBs) is rinsed with clean water. Furthermore, the volume displacement of 16 PWBs is approximately 0.4 ft^3 (= 2.9 gallons). Therefore the volume of the rinse tank is 162 times larger than the volume displacement of the PWBs for rinse tank 1 in the automated electroplating wet process line. Taking these observations into consideration, if rinse tank 1 volume was 20 gallons and the water flow rate was 2 gpm, then one out of 10 lots instead of one out of 28 lots would be rinsed with clean water and water consumption would be reduced by 66%. Annual water reduction would be 15.7 million gallons (43,200 gallons/day). Finally, once acceptable water quality is determined, in-line recycling and reclaim can be used to further reduce water consumption. Calculations provided by Don Hoppe indicate that total water use can be reduced by 42% using in-line water recycling and reuse.

The water up flow rate in all rinse tanks in the electroplating wet process line are maintained at 6 gpm whether the rinse tank is processing lots or not. One reason to maintain flow rates in rinse tanks that use ultrapure water (UPW) is to reduce bacteria formation, which can adhere to product surfaces and reduce yield. Detailed studies in the Semiconductor Industry have shown that UPW flow rates between 0.2 and 0.5 gpm are sufficient for preventing bacteria formation in UPW. Assuming the rinse tanks in the two automated lines are processing 75% of the time, implementing idle flow rates of 0.5 gpm would result in water use reductions of 7.3 million gallons per year (20,000 gallons/day). This value for water savings is determined by the following calculation:
*Water Savings = 5.5 gpm*60 min*6 hours/day*365 days*10 rinse tanks = 7.3 million g.*

These observations lead to the following recommendations for water use and waste stream reduction:

1. Implement idle water flow rate of 0.5 gpm in all dynamic flow rinse tanks. Upon discussion with the Hadco team, this project could be implemented.
2. Reduce rinse tank volumes and correspondingly reduce water flow rates.

Such a significant reduction of tank volume is not applicable on the existing tank lines, as the racks will not fit in the tanks. Also, the positioning system would have to be very precise to keep the board in position with no swing or movement to apply this theory. It is not cost effective to retrofit the existing system to the lowest water volume suggested.

However, this theory may be applicable to reducing the tank volume to some degree. In addition, this suggestion can be part of new line discussions.

3. Consider in-line water recycling and reuse for electroplating wet process lines. This suggestion is feasible with proper study and design.
4. Implement four-sided rinse tank drain for improved rinse efficiency by convection.

Unfortunately, the size of the racks on the current system would not support implementation of this idea on existing lines. However, this suggestion could be applied to design discussions for new lines.

5. Increased throughput and capacity of line - Current technology does not support

additions to the process lines that will increase capacity. However, this idea can be employed in future line design discussions.

Manual Electroplating Line

The manual electroplating line has the same process flow as the automated electroplating line. The rinse tank volumes are 100 gallons, the water up flow rate is 3 gpm and 8 PWBs are rinsed at a time. Water drains out of the top of the rinse tanks from one-side. All of the observations and recommendations made for the automated rinse tanks apply to the manual rinse tanks. There are some differences in water consumption to be noted:

1. The ratios of manual rinse tanks volume to PWBs volume are 69:1, while the same ratios for automated rinse tanks are 126:1.
2. The up flow rate in the manual tanks is only 3 gpm compared to 6 gpm in the automated tanks.
3. Water in the manual rinse tanks is turned over once every 33 minutes, compared to once every 70 minutes in the automated rinse tanks.

These observations show that although the manual rinse tanks have margin for optimization, they use water more efficiently than the automated benches. However, implementation of reduced rinse tank volumes, decreased process flow rates from 3 gpm to 2 gpm and use of idle flow rates (0.5 gpm) will lead to significant reductions in water use and waste stream reduction. For example, assuming the rinse tanks are idle 50% of the time, implementing idle flow rates would reduce water consumption by 7.9 million gallons per year (21,000 gallons/day).

This value for water savings is determined by the following calculation:

*Water Savings = 2.5 gpm*60 min*12 hours/day*365 days*12 rinse tanks = 7.8 million g.*

Reduced tank volumes may not be feasible due to rack size constraints. Changes to idle flow rates and reduced process flow rates will be implemented after proper study and design.

5. Hadco Santa Clara Report 2

Site Visit Report for Water Use Reduction

Hadco Corporation, Santa Clara, CA

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September 7, 1999

The Silicon Valley Manufacturing Group supported this work.

Executive Summary

The objective of this program is to realize gains in performance improvements, cost savings and environmental concerns by reducing point-of-use water consumption. This report represents observations and recommendations determined from the initial site visit to the Water Treatment and Inter-layer Wet Process Area at Hadco's Santa Clara site. Specific observations for water use reduction include:

1. Implementation of idle flow rates and reductions in process flow rates in spray rinses and rinse tanks. Estimated water reduction is 95,000 gallons per day.

2. Determine water quality in rinse tanks and spray rinse tools as a function of rinse time using detailed conductivity data. This data can be used to optimize rinse processes and also to determine waste stream segregation for recycling/reclaim.

2. Observations and Recommendations

The findings in this report are based on interviews with Jaime Mendoza (Water Treatment Manager), Don Howell (Engineering Manager/Multilayer Group) and Kulwant Cheema (Sr. Process Engineer) and site visits to the water treatment facilities and multilayer wet process areas. These interactions revealed opportunities for introducing new technologies for improved cost effective waste treatment, metrologies for detection of total-oxidized organic carbon (TOC) contamination, use of detailed conductivity data in rinse tanks for waster stream segregation, and opportunities for reducing water consumption.

Water Treatment Facilities

The water treatment facilities at Hadco, Santa Clara are sophisticated automated systems with some remote sensing capabilities. Currently, automatic bypass valves are used to segregate waste streams from rinse tanks that have conductivity greater than 2000 µS/cm. At current water use, typical conductivity values from buildings B and C range from 400µS/cm – 800µS/cm. This indicates that there is significant margin for reducing water use in rinse tanks and increasing contaminant concentrations in rinse waters, while maintaining current recycling/reclaim capabilities. However, the current conductivity sensing capability provides the total conductivity from the entire building. Conductivity values of rinse water used in specific processing tools are not known. However, as demonstrated in the Semiconductor Industry, this type of information is highly useful for determining waste stream segregation, optimizing rinse processes and trouble shooting wet process tools. Therefore, it is recommended that the baseline conductivity behavior as a function of rinse time be determined for each wet process tool in the electroplating and interlayer areas.

Technologies used in recycling/reclaim in the Semiconductor Industry that may be useful to Hadco include Electrodeionization (EDI) and real-time TOC detection. Russ Parker of

Hewlett-Packard Labs in Palo Alto (650 857 3383) has used an EDI system from Ionics for recycling ultrapure water with acid, basic and metal contamination. A publication by R. Parker is included in Appendix III. Real-time TOC detection can be accomplished using a Sievers TOC analyzer. The Sievers instrument has a 47-second sampling rate.

Recommendations

1. Acquire conductivity as a function of rinse time for all rinse processes in wet electroplating and interlayer areas.
2. Investigate feasibility of EDI for water treatment.
3. Determine usefulness of real-time TOC analysis for water treatment.

Interlayer Wet Processing Area

The process flow in Preclean (Panel Prep) includes the following steps:

1. Aluminum oxide polish
2. Spray Rinse
3. Acid Clean, 18% Sulfuric/Nitric/Phosphoric Acid at 100 °F.
4. Spray Rinse
5. Hot Air Dryer

In the near future, the Aluminum oxide polish step will be eliminated leaving optimization of the Acid clean and subsequent rinse step. The first step in spray rinse optimization for water-use reduction is to implement idle flow rates. Each tool currently uses 8 gpm of water and has 30% idle time. If idle flow rates of 0.5 gpm were incorporated for all 7 tools, annual water savings would be:

*7 tools*7.5 gpm*60 min*7.2 hours*365 days = 8.3 million gallons (22,680 gallons/day)*

Kulwant Cheema already has a plan to install sensors in these tools that will implement idle flow rates and realize these water use reductions. The rinse process water flow rate is 8 gpm. At a product linear transfer rate of 2.5-meters/min and product size of 0.5 meters, 1.6 gallons of water is used to rinse Acid from each piece. It has been shown in the semiconductor industry that as little as 0.25 gallons of water per piece can be used to rinse sulfuric acid residue. In fact, new tools now being installed at Hadco will use 2 gpm which is about 0.4 gallons of water per piece for post-Acid Clean rinsing. Implementation of 2 gpm rinse process in the 7 tools that now use 8 gpm, would result in annual water savings of:

*7 tools*6 gpm*60 min*16.8 hours*365 = 15.4 million gallons (42,000 gallons/day)*

Implementation of a 2-gpm-rinse process flow rate may require design modifications to the spray geometry.

Recommendations

1. Kulwant Cheema's plan to implement idle flow rates using sensor technology in 7 wet process tools is consistent with best practices in the Semiconductor Industry.
2. As discussed with Kulwant Cheema, reduction of rinse process flow rates from 8 gpm 2 gpm should be explored. This may require some equipment modifications to the spray nozzle geometry and will also require product quality assurance validation.
3. The chemistry, temperature and process time of the Acid Clean and the rinse water temperature, water flow rate and rinse cycle time of the post-Acid Clean rinse process should be optimized. Appendix II outlines a Plan for Rinse Optimization and Validation that can be adapted to applications for optimizing the Acid Clean process and the post-Acid Clean rinse process.

Oxide Area

The process flow in the Oxide area had the following steps:

1. Sodium Hydroxide Clean (Tank # 19)
2. Rinse (Tank #20)
3. Sulfuric Acid (#22)
4. Micro-etch
5. Rinse (Tanks #27 then # 28)
6. Predip (Tank #17)
7. Oxide Bath (Tank #15 and #16)
8. Rinse (Tank #14 then Tank #13)
9. Post Dip
10. Rinse
11. Dry

This process flow includes rinse processes at steps number 2, 5, 8 and 10. The rinse tanks used in steps number 8 and 10 have flow rates of about 10 gpm. Assuming 75 % utilization, implementation of idle flow rate of 0.5 gpm in this tank would result in annual water savings of:

*2 tanks*9.5 gpm*60 min*6 hours*365 days = 2.5 million gallons (6840 gallons/day)*

Furthermore, the fluid flow design of the tank sue in step 10 has the water inlet almost directly above the drain. This means that water introduced into the tank is not circulated over the product. In the current geometry, poor rinse efficiency is expected.

Tank 5 has a water flow rate of 11-13 gpm. An idle flow rate of 0 gpm is supposed to be activated when this tank is not processing product. However, due to a malfunction, the tank's idle flow rate was 11-13 gpm. Assuming 75% utilization, implementation for the idle flow rate would result in annual water savings of:

*12 gpm*60 min*6 hours*365 days = 1.6 million gallons (4320 gallons/day)*

The rinse process flow rates in several of the rinse tanks are relatively high at 10-13 gpm. Reducing these flow rates to 6 gpm would result in annual water savings of:

*3 tanks*6 gpm*60 min*18 hours*365 days = 7 million gallons (19,440 gallons/day)*

Recommendations

1. Implement idle flow rates.
2. Implement improved fluid dynamic design in rinse tank used in step 10.
3. Implement improved fluid dynamic design of four –sided overflow in all rinse tanks.
4. Investigate the impact on product quality of reducing rinse process flow rates to 5-6 gpm from 10-13 gpm.

6. MMC Technology Report

Site Visit Report for Water Use Reduction

MMC Technology

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Supported by the Silicon Valley Manufacturing Group

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1. Executive Summary

This document reports results from an evaluation of disc cleaning and rinsing processes at MMC Technology, San Jose, CA during September 1999. The specific objectives of the project were to increase performance, reduce product costs, and reduce chemical, Ultrapure Water and energy consumption. The findings in this report are based on site visits to MMC Technology plating, stripping and cleaning areas.

The standard rinse strategies and ultrapure water (UPW) use were evaluated by initiating the first two phases of a four-phase program designed to reduce UPW consumption and rinse cycle times in semiconductor manufacturing (Appendix II). Complete implementation of this program in the semiconductor industry has resulted in significant cost savings and increased product throughput.

Conductivity measurements were used to determine the rinse effectiveness in wet tools used for plating and post-Texture cleaning processes. These results indicate that rinse times and UPW consumption may be reduced by approximately 30 to 50% in these tools. This could also lead to a reduced number of post-texture cleaning steps as well as to an increase in overall factory throughput. Similar opportunities exist for some of the rinse processes in the wet plating line. Details are provided in this report.

All recommendations made here are based on rinse water conductivity measurements and should be validated by appropriate disc surface analysis before implementation of optimized rinse processes. In this way, the effect, if any, of optimized rinse processes on disc surface quality and device characteristics can be determined.

Examination of the overall process flow to determine a complete set of opportunities for reducing cycle times and UPW consumption were outside the scope of this project. Based on work performed at similar manufacturing facilities, there can be considerable improvement in disc throughput, overall process times and application of appropriate metrologies for quality control and quality assurance.

2. Conductivity Results

Wet Plating Line

Post-Acid Etch Rinse

Figure 1 shows conductivity and UPW consumption plotted as a function of rinse time for post-Acid Etch rinse of about 1200 3.5 inch diameter discs. The standard rinse process includes spray rinse, followed by transfer to a dragout "dunk" tank. After the dragout, the dunk tank is purged. Total UPW consumption for this rinse process is 105 gallons per 1200 3.5-inch discs.

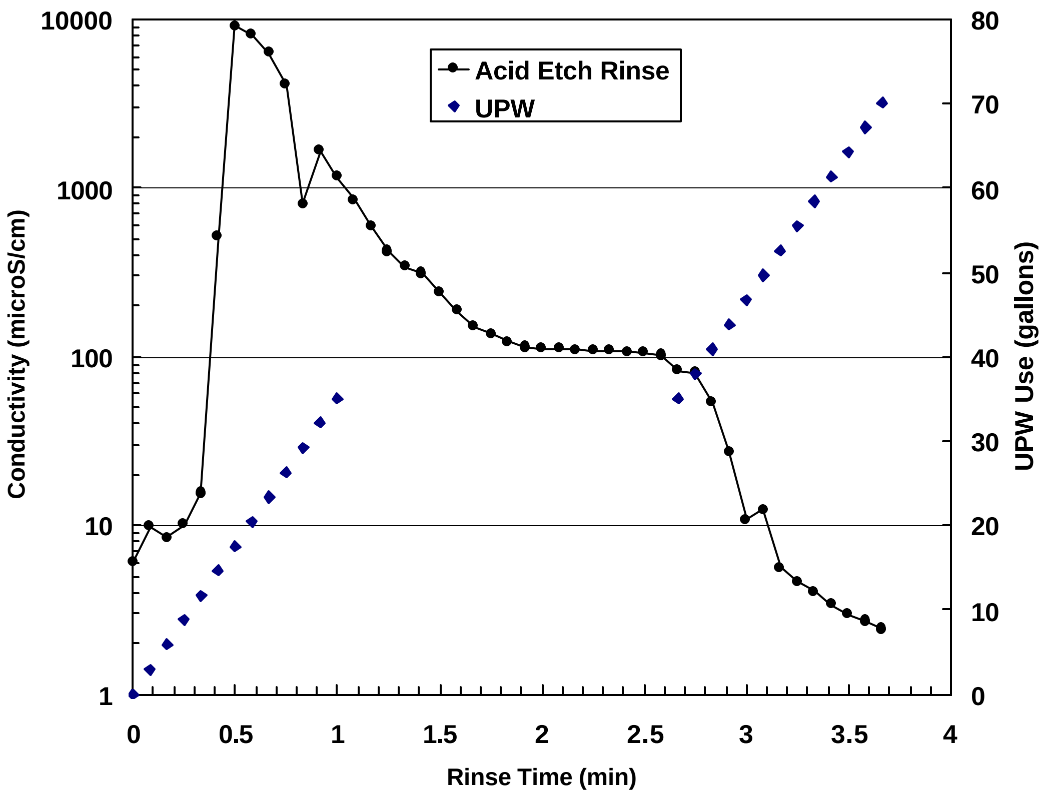

Figure 1. Conductivity and UPW consumption plotted as functions of rinse time for post acid etch rinse. Conductivity is plotted on logarithmic scale.

The conductivity did not change significantly during the dragout segment of the rinse. The spray rinse process was clearly more effective than the dragout tank. This indicates that the dragout segment may not be effective for removing chemical residue from disc surfaces and the disc holding rack. Elimination of this segment would reduce rinse time and UPW consumption by approximately 30%. These recommendations need to be validated by disc surface analysis to determine what effect, if any optimized rinse processes have on disc surface quality and on device properties.

Post-Zincate 1 Rinse

Figure 2 shows conductivity plotted as a function of rinse time for post-Zincate 1 rinse of about 1200 3.5-inch diameter discs. The standard rinse process includes spray rinse, followed by transfer to a dragout "dunk" tank. After the dragout, the dunk tank is purged. Total UPW consumption for this rinse process is 105 gallons per 1200 3.5-inch discs.

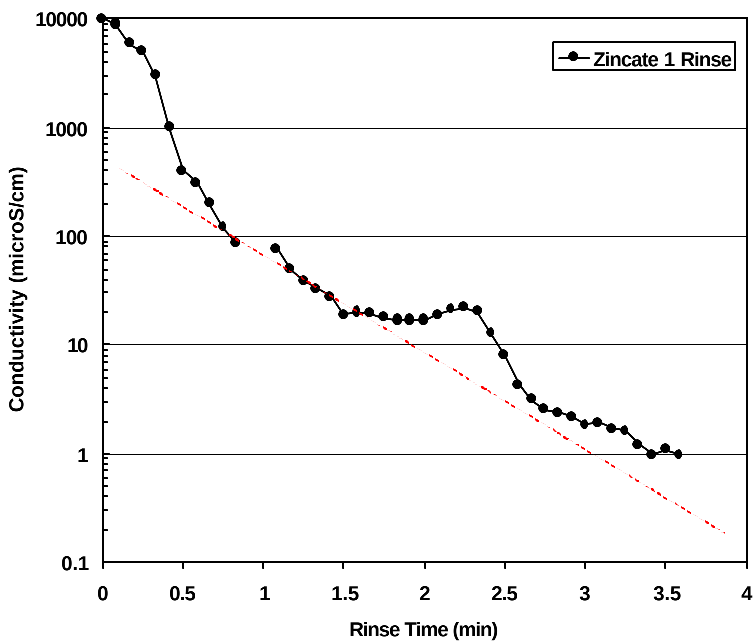

Figure 2. Conductivity is plotted as a function of rinse time for post-Zincate 1 rinse. Conductivity is plotted on logarithmic scale.

The conductivity did not change significantly during the dragout segment of the rinse. The dashed redline indicates a trend in contamination removal during spray rinse processing. This indicates that the dragout segment may not be effective for removing chemical residue from disc surfaces and the disc holding rack. The data indicates that spray rinse is more effective for contamination removal than the dragout tank. Elimination of the dragout segment would reduce rinse time and UPW consumption by approximately 30%. These recommendations need to be validated by disc surface analysis to determine what effect, if any optimized rinse processes have on device properties.

Post-Zincate 2 Rinse

Figure 3 shows conductivity plotted as a function of rinse time for post-Zincate 2 rinse of about 1200 3.5-inch diameter discs. The standard rinse process includes spray rinse, followed by transfer to a dragout "dunk" tank. After the dragout, the dunk tank is purged. Total UPW consumption for this rinse process is 105 gallons per 1200 3.5-inch discs.

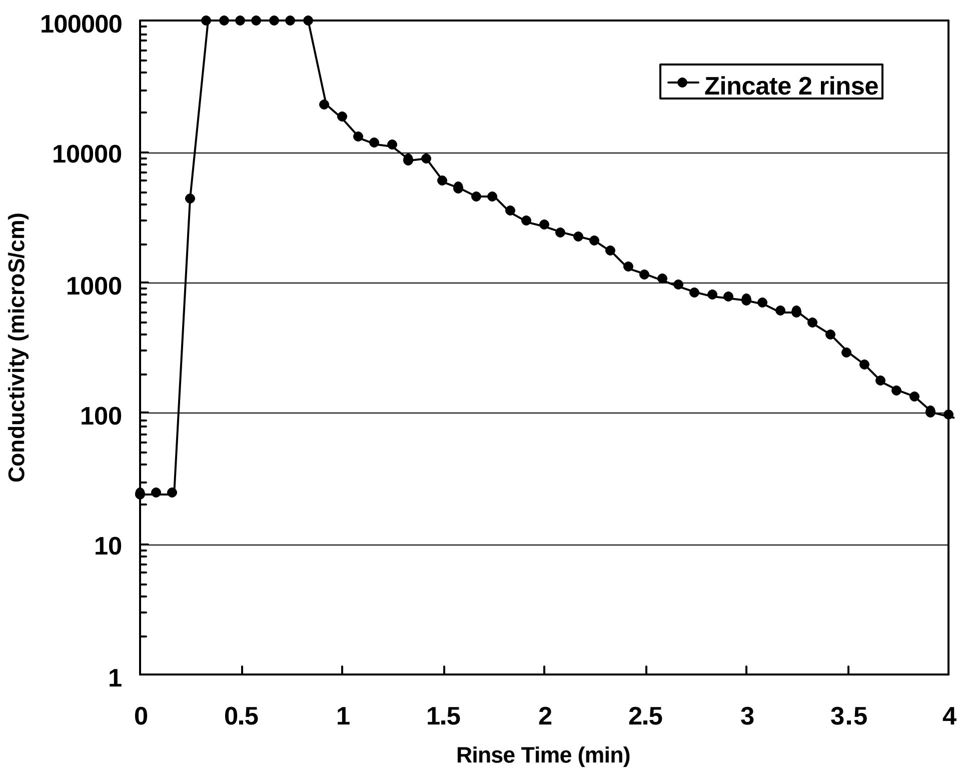

Figure 3. Conductivity is plotted as a function of rinse time for post-Zincate 2 rinse.

The conductivity data indicates that either the post-Zincate 2 rinse does not effectively remove chemical carryover from disc surfaces and disc holding rack, or that reduced rinse times and UPW use may have little effect on device properties. These recommendations need to be validated by disc surface analysis to determine what effect, if any optimized rinse processes have on device properties.

Post-Ni Rinse

Figure 4 shows conductivity plotted as a function of rinse time for post-Ni rinse of 1200 3.5-inch diameter discs. The standard rinse process includes spray rinse, followed by transfer to an overflow rinse tank. Total UPW consumption for this rinse process is 90 gallons per 1200 3.5-inch discs.

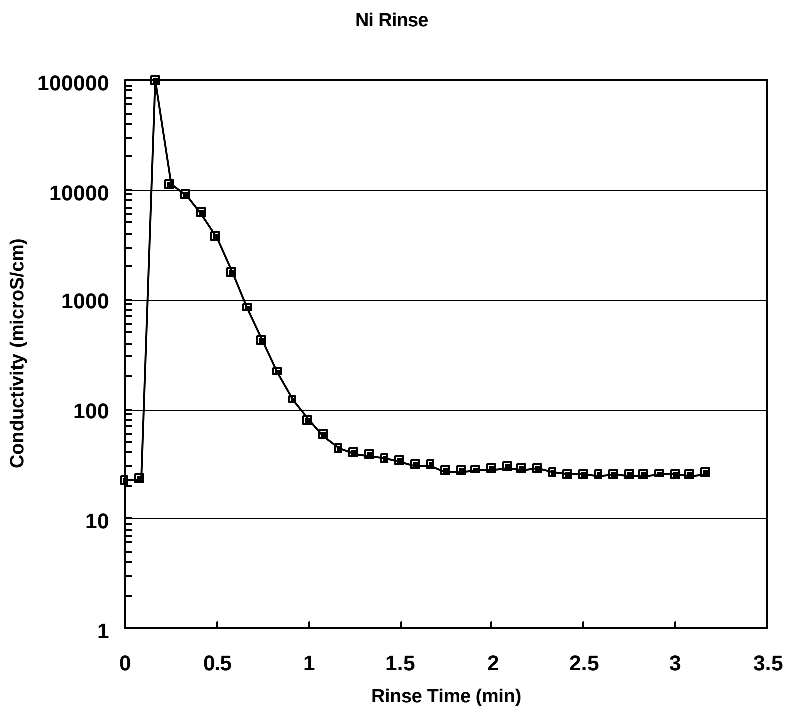

Figure 4. Conductivity is plotted as a function of rinse time for post-Ni rinse.

The conductivity data indicates that the post-Ni rinse is completed after the first 1.5 minutes. If the existing rinse time were reduced, UPW savings could be about 20% lower. In addition, UPW flow rate in the overflow tank can probably be reduced. These recommendations need to be validated by disc surface analysis to determine what effect, if any optimized rinse processes have on device properties.

Post-Texture Cleaning

A simplified disc process flow at MMC Technology (San Jose) includes:

PLATING – POLISH – TEXTURE – CLEANING.

Post-texture cleaning is performed in a series of two wet stations. The first includes chemical cleaning and rinsing, and the second is equipped with a series of cleaning steps. Disc surface quality control concerns include particles, scratches, slurry, and surfactant residues. The two wet benches employ different chemistries, providing a two-step, two-tool process to achieve complete cleaning for the various surface contaminants.

Conductivity readings for rinse stations on the first tool indicated that the rinse process is not very effective at removing carryover contaminants, based on the relatively high conductivity of wastewater at the end of the rinse cycle. Since the inefficient rinsing appears to have no affect on product yield, it was surmised that one approach to reducing water usage in the tool would be to combine both post-texture cleaning processes into one (the second and more efficient) tool. Potential wastewater savings would amount to approximately 40 gpm by implementing this approach. Added benefits of increasing production floor space, and relieving crowded conditions in the production area, would also be enjoyed. However, this recommendation potentially requires significant re-tooling expense that may be cost-prohibitive to implement. In addition, disc surface analyses on a prototype tool, and product requalification, would be required to assess what effect, if any, the process change produced.

Conductivity readings for the second disc cleaning process tool indicated no change in conductivity in the final rinse stations. The high quality of wastewater from the process had already been investigated by MMC, and work was underway at the time of the study to re-plumb wastewater from clean rinse tanks to the front end of the tool where less clean processes occur. At the time of this report, tool re-plumbing has been completed for all process tools for a net reduction in UPW of 44.8 gpm. Further investigation into reuse of wastewater, reduction of fresh make-up UPW water, or reducing the number of rinse steps is warranted. These have the potential to reduce process cycle times, and improve disc throughput, leading to additional cost-savings by reducing the number of tools, and increasing overall factory throughput. Conductivity data indicates that the number of rinse tanks for the existing process could be reduced from three to one, and rinse times reduced to up to one-half for a full lot of discs.

The re-use of existing wastewater, and potential reduction in the number of rinse stations, and process cycle times, are the first steps in reducing wastewater from the post-texture disc cleaning process. A second alternative involving the combining of two wet stations presents a significant process change with potential to dramatically reduce wastewater usage, processing time, and improve factory conditions. These recommendations require validation by disc surface analysis, and vendor qualification, to determine whether they are economically feasible. The short life cycle of most magnetic media products, coupled with the time-consuming process to qualify products, suggests that these options should be explored in new product development rather than for existing manufacturing processes.

7. Agilent Technologies Report

Rinse Water Optimization at Agilent Technologies

Prepared By

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And
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1. EXECUTIVE SUMMARY

The objective of this work is to enhance performance, realize cost savings and reduce ultrapure water (UPW) consumption through rinse process optimization and overall ultrapure water use management. This is accomplished through a four-phase program to:

1. Evaluate standard rinse processes by measuring the important rinse parameters in production wet tools. These include; detailed conductivity measurements made during rinse, UPW flow rates, temperature, megasonic agitation, tank geometry, overhead spray showers, drain time, wafer transfer time, pullout velocity, etc.
2. Make initial recommendations for optimized rinse processes based on data collected in phase 1.
3. Validate initial recommendations for optimized rinse processes using conductivity measurements of rinse water and wafer surface analysis such as light point defect (LPD), total x-ray reflectance fluorescence (TXRF) and time-of-flight-SIMS (ToF-SIMS).
4. Final validation and effect of optimized rinse processes on device electrical properties

This report includes work completed on Phase 1 and 2 at Agilent Technologies. Implementation of recommendations made in this report could lead to 50% reductions in rinse cycle time and about 50-80% reductions in UPW consumption. All recommendations are based on conductivity measurements alone and need to be validated by wafer surface measurements to determine what effect, if any optimized rinses have on wafer surface quality. A detailed optimization plan is outlined in appendix II.

1. Optimization of Rinse Processes

Wet Bench DSW 30

Figure 1 shows conductivity and ultrapure water (UPW) consumption plotted as a function of rinse time for post-sulfuric acid/hydrogen peroxide mix (SPM) rinse of 25, 6-inch wafers. The standard rinse process consisted of an initial 2-minute overflow segment followed by 5 overflow dump rinse (OFDR) cycles. The OFDR rinse included 21-second overflow segments and 5-second drain time. The total UPW use was 190 liters per 25, 6-inch wafers. Of the total UPW use about 152 liters, or 80%, is used during overflow. Conductivity data shown in Figure 1 indicates that the overflow segments are not as effective as the dump/fill cycles for removing chemical residue form wafer surfaces.

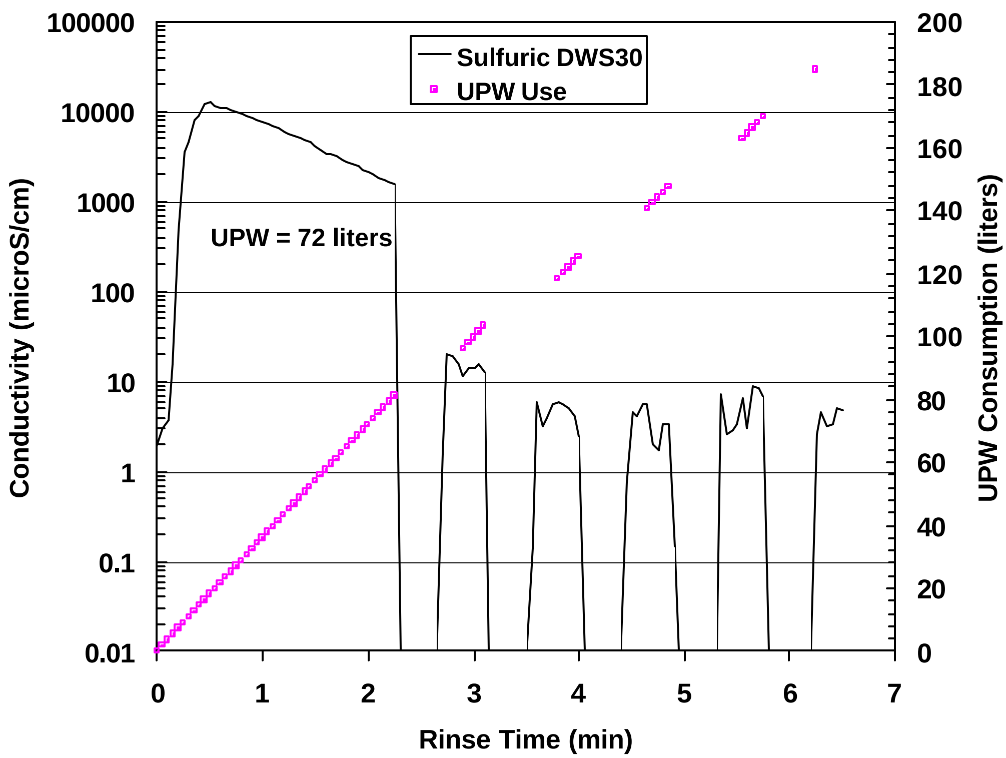

Figure 1. Conductivity and UPW consumption are plotted as a function of rinse cycle time for time post-SPM rinse of 25, 6 inch-diameter wafers.

Based on these measurements, the UPW can be reduced by 50-80% by reducing or eliminating the overflow rinse segments. This would also reduce rinse cycle time by as much as 3.4 minutes.

Figure 2 shows conductivity and ultrapure water (UPW) consumption plotted as a function of rinse time for post-HF rinse of 25, 6-inch wafers. The standard rinse process consisted of a 5-minute overflow rinse and consumed about 180 liters of UPW per 25, 6-inch wafers. This standard rinse is typical for rinsing after etching chemicals, like HF, where particle contamination on bare silicon surfaces is a concern. There are no recommendations for optimization of this rinse process based on the conductivity data and on data collected at other semiconductor manufacturers.

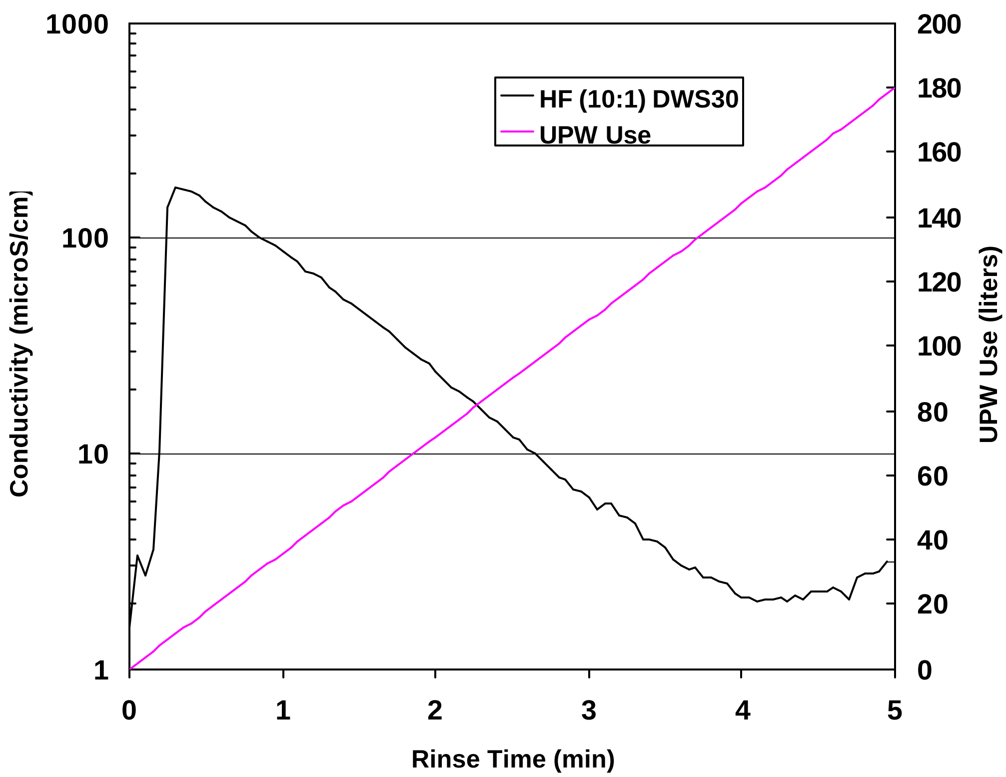

Figure 2. Conductivity and UPW consumption are plotted as a function of rinse time for post-HF rinse of 25, 6-inch diameter wafers.

Sputter Area

Figure 3 shows conductivity and UPW consumption plotted as a function of rinse cycle time for post-SPM and post-HF rinses of 25, 6-inch wafers. The standard OFDR rinses consisted of 5 cycles with 21-second overflow segments and 5-second drain time between cycles. The overflow segments accounted for 105 seconds of rinse time and about 71 liters of UPW for each rinse. Elimination of the overflow segments could save about 1.5 minutes of rinse time and 71 liters of UPW per 50, 6-inch wafers for HF rinse and 1.5 minutes of rinse time and 71 liters of UPW per 50, 6-inch wafers for SPM rinse.

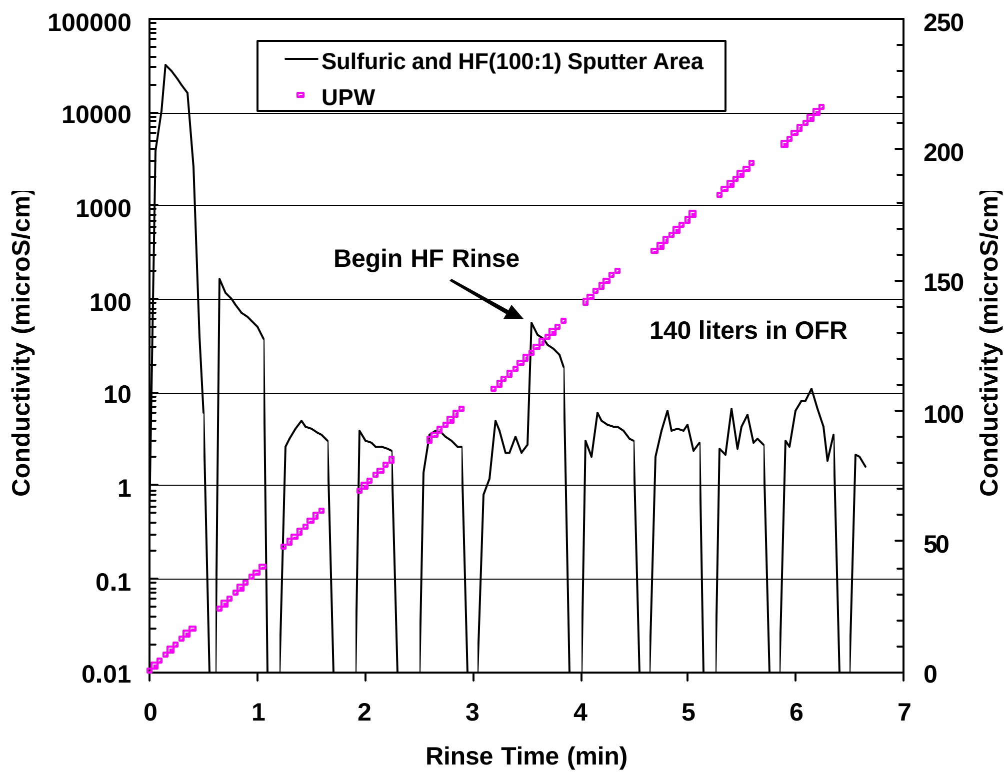

Figure 3. Conductivity and UPW Use are plotted as a function of rinse time for post-SPM and post-HF rinses of 25, 6-inch wafers.

Mask Area

Figure 4 shows conductivity and UPW consumption plotted as a function of rinse cycle time for post-BOE rinse of 25, 6-inch wafers. The standard OFDR rinses consisted of 5 cycles with 12-second overflow segments and 5-second drain time between cycles. However, the rinse tank did not completely empty during the 5-second drain segments. It is recommended that the tank be completely emptied during the drain segments. This may be accomplished by increasing the drain time from 5 seconds to 8 – 10 seconds.

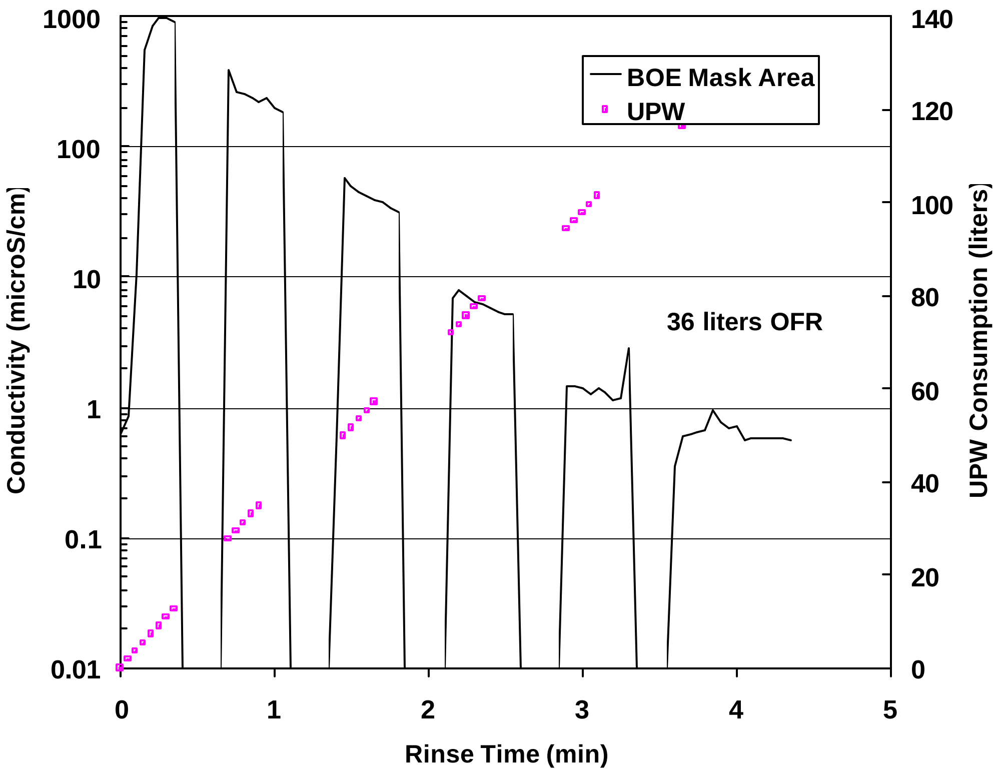

Figure 4. Conductivity and UPW Use are plotted as a function of rinse time for BOE rinse of 25, 6-inch wafers.

Figure 5 shows conductivity plotted as a function of rinse time for three post-BOE rinse strategies; overflow dump rinse (OFDR) with 5-second drain time (blue line, same as Figure 4), OFDR with 10-second drain time (red line) and quick dump rinse (QDR) with 10 second drain time (black line). Both rinse strategies with 10-second drain time performed better than the rinse with 5-second drain time. The 10-second drain time rinses reached the baseline conductivity after 2 rinse cycle steps while the 5-second drain time rinse reached the baseline conductivity value after 5 rinse cycle steps.

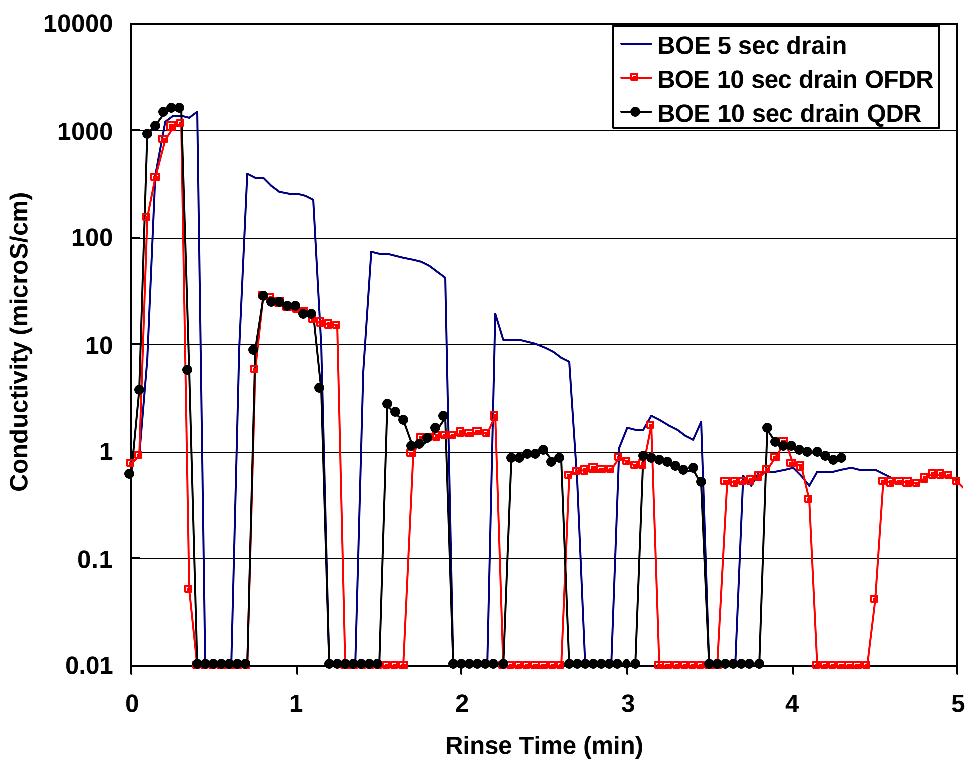

Figure 5. Conductivity is plotted as a function of rinse cycle time for post-BOE rinses of 50, 6-inch diameter wafer.

Figure 6 shows a comparison of UPW use for the rinse processes shown in Figure 5. The QDR process consumed 87.6 liters per 50 wafers while the OFDR processes consumed about 117 liters of UPW per 50 wafers. Furthermore, the QDR process could be reduced from 5 to 4 QDR cycles reducing UPW consumption to about 75 liters per 50 wafers.

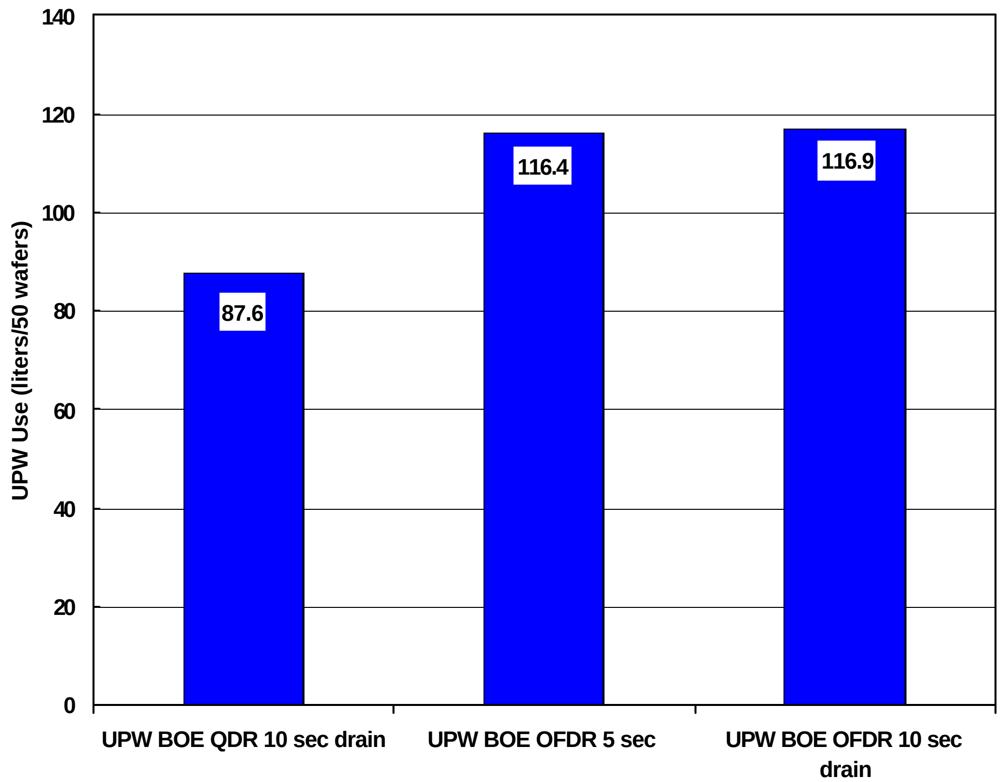

Figure 6. UPW Use is shown for OFDR and QDR processes shown in Figure 5.

Epi Area

Figure 7 shows conductivity and UPW consumption plotted as a function of rinse cycle time for post-HF (1:1) rinse of 25, 6-inch wafers. The standard quick dump rinse (QDR) rinses consisted of 10 cycles and 5-second drain time between cycles. The conductivity reached the baseline value after 5 QDR cycles.

The conductivity data indicates that reducing the number of QDR cycles from 10 to 5 may optimize this rinse. This would reduce UPW consumption and rinse cycle time by 50%.

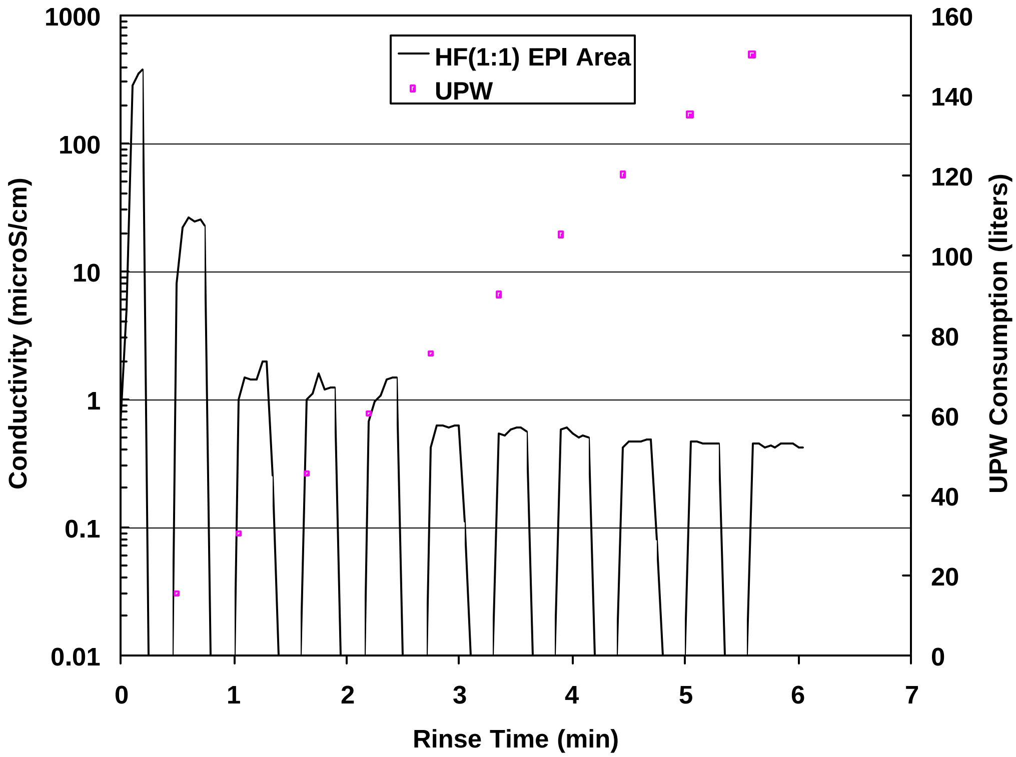

Figure 7. Conductivity and UPW Use are plotted as a function of rinse time for HF (1:1) rinse of 25, 6-inch wafers.

Mask Area

Figure 8 shows conductivity plotted as a function of rinse time for three post-SPM rinse strategies. The conductivity data indicates that overflow segments do not have a significant effect on rinse effectiveness. Based on the conductivity results and benchmarking data it is recommended that a 4 or 5 cycle QDR process be implemented for post-SPM rinse. A five-cycle QDR process would consume about 75 liters of UPW per 50 wafers.

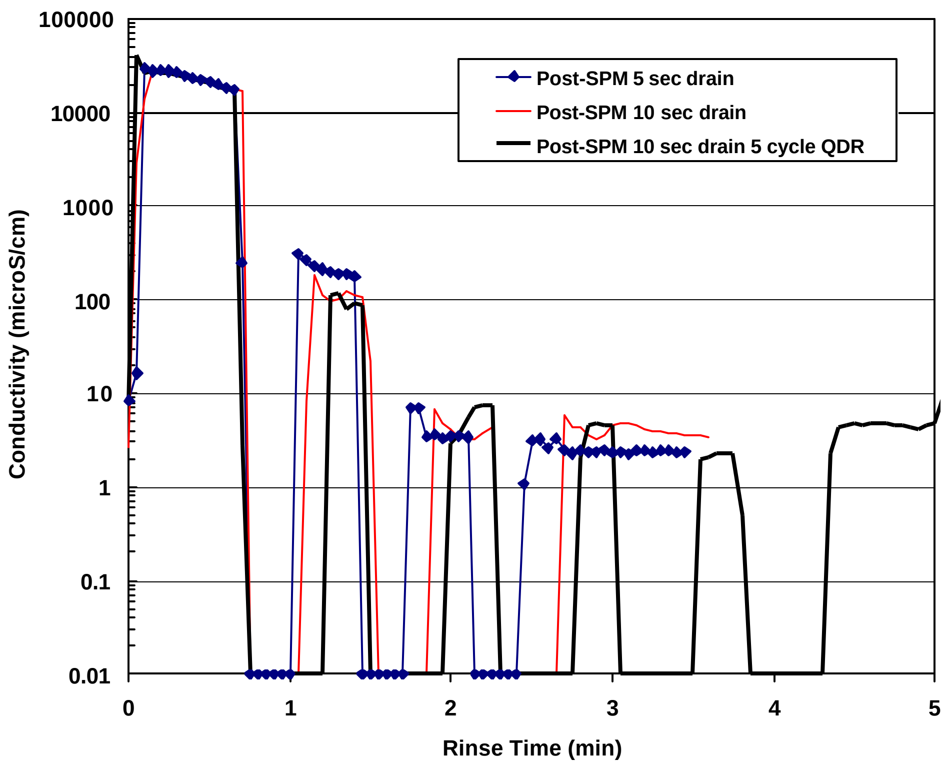

Figure 8. Conductivity is plotted as a function of rinse time for three post-SPM rinse processes.

2. Summary

Conductivity data indicates that for post-SPM and post-HF rinses, cycle times can be reduced by about 50% and UPW consumption can be reduced by 50 – 80%. The post-BOE rinse tank was not draining completely. Conductivity data showed that rinse effectiveness is improved by increasing the drain time from 5 seconds to 10 seconds between OFDR cycles. It is recommended that a 4-cycle QDR process be implemented for post-BOE rinse. This would reduce UPW consumption for post-BOE rinse by 50%. Conductivity measurements indicate that the number of QDR cycles for post-HF (1:1) rinse can be reduced from 10 to 5 or 6 cycles. This would reduce UPW consumption and rinse cycle times by as much as 50%.

8. Summary and Recommendations

Manufacturing of high technology products like semiconductors, disk drives and printed wiring board continues to be an essential part of the South Bay economy. The cleaning and rinsing processes in the manufacturing of these devices and other high tech products (like flat panel display) consumes significant amounts of water. This poses challenges to both the cost of manufacturing costs and impact on local environment. An obvious solution and the approach taken here are to reduce point-of-use water consumption. In this way, manufacturing costs can be reduced and significant environmental benefits can be realized. Reducing point-of-use water consumption is nontrivial as changes in cleaning and rinsing processes can have a deleterious effect on device performance and yield. To address these concerns, a detailed plan for the evaluation and implementation of optimized cleaning and rinsing strategies has been developed. The methodology and best practices for rinse optimization were transferred to MMC Technology, Hadco Santa Clara, and Agilent Technology. Site visits to MMC, Hadco and Agilent showed implementation of optimizations would lead to annual reductions in ultrapure water consumption of 42.6 million gallons and direct cost savings of at least $4.26 million. Intel has been aware of this technology for some time and has already implemented rinse strategies for reduction of ultrapure water (UPW) in its factories around the world. Based on these practices, Intel is a leader in the Semiconductor Industry for optimization of water use. Other areas in the manufacturing process where Intel may benefit from reductions in point-of-use UPW consumption were also discussed. These opportunities are outside of the San Francisco Bay Area and outside of the scope of the work presented here. Development and implementation of these opportunities necessitate close working relationship with tool suppliers, specifically suppliers for chemical-mechanical polishing tools. These relationships are in place and significant progress is being made to determine other opportunities for reducing UPW consumption in Semiconductor Manufacturing.

Most of the recommendations made in this report are based on conductivity measurements and observations of the mechanical design and fluid dynamic performance of wet tools. This essentially covers the first two phases of the plan outline in Appendix II. These recommendations should be validated by product surface measurements to determine what effect, if any optimized rinse strategies have on product surface quality and ultimately on device performance. However, some recommendations are based only on the water use management in wet tools. These optimizations do not require additional validation. Next steps for this program may include 1. Helping companies implement recommendations made in this report, 2. Applying methodology to other companies not included in this report and 3 to other high tech manufacturing sectors (e.g. flat panel display). The best opportunity to implement reductions in water use is when factories are first built or upgraded. During these times, new tools are installed and new processes are qualified. It is much less expensive and time consuming for manufacturers to qualify changes in rinsing and cleaning during tool installation than after a manufacturing process flow has been qualified and devices are being made.

Appendix I: Summary Literature Review

Year	Author	Contribution
1959	Tallmadge, Walker	Ideal mixing, still and running rinses
1962	Tallmadge, et. al.	Diffusion model – concludes other mechanisms present
1990	Nakao, et. al.	Trench rinsing – concludes diffusion dominant mechanism of removal
1992	Tonti	1-D diffusion from hydrodynamic boundary layer into perfectly stirred bulk
1993	Helms, Rosato, et. al.	Convective/ideal mixing model; experiments show rinse is more than diffusion from hydrodynamic B. L.
1994	Christenson	Comparison between immersion and spin rinsing
1995	Helms, et. al.	Analysis of mechanisms involved in rinsing – foundation of current model development approach
1995	Parker, Verhaverbeke, et. al.	Analysis of macro and microscale (including trench) rinse considerations; comparison between immersion and plug flow rinsing
1995-1996	Rosato, et. al.	Consideration of design parameters to optimize rinse efficiency; fluid dynamic analysis of wafer rinsing
1996	Roche, Peterson, Hansen	Effects of rinse volume, wafer spacing, and pulsed flow on rinse effectiveness; immersion strips off chemical from surface
1997	Christenson	Reviews rinse processes with respect to water usage, theory behind various rinse factors
1997	Olim	Reviews wetting, cleaning, rinsing, and drying of trenches; sites diffusion as dominant removal mechanism, convection influences ∇c
1997	Chiarello	Methodology for Optimizing post-SPM Rinse Process in Semiconductor Manufacturing
1998	Parker, Chiarello and Gomez	New Rinse Strategy for Rinsing in Front-End-of-Line Surface Prep, Semiconductor Manufacturing
1998	Tritapoe and Chiarello	Optimization of SC1 and SC2 Rinse Processes in Semiconductor Manufacturing

1999	Chiarello	Rinse Optimization for Next Generation Wet Tools
1999	Romero, Sief, Hebda, Chiarello and Peterson	Fundamentals of Rinse Processes for Semiconductors

Appendix II: Validation, Demonstration, and Implementation Plan

1.0 Phase 1: Diffusion Wet Tool Water Use Audit & Baseline Characterization
- 1.1 Water Use Audit
    - 1.1.1 Wet Tool Design Information Documentation (Tank Volumes, PullOut Rates, Transfer Times, and Possible Modes of Operation and Flow Rates).
    - 1.1.2 Rinsing Response Surface Calculations.
    - 1.1.3 Report on Calculated Baseline Performance and Recommendations for Optimized Processes.

2.0 Baseline Characterization
- 2.1 Installed Sensor Evaluation.
- 2.2 Recommendations for Sensor Upgrades if Necessary.
- 2.3 Sensor Installation and Calibrations.
- 2.3 Baseline Calibrations.
    - 2.3.1 Rinse to Resistivity
    - 2.3.2 Analysis of Particle Counts
    - 2.3.3 Analysis of Surface Residues
    - 2.3.4 Chemical Analysis of Down Stream Baths
- 2.4 Comparisons to Predictions.

3.0 Phase 3: Optimization
- 3.1 Final Recommendations for DOE on Rinse Optimization.
- 3.2 Evaluation 1
    - 3.2.1 Rinse to Resistivity
    - 3.2.2 Analysis of Particle Counts
    - 3.3.3 Chemical Analysis of Down-Stream Baths
    - 3.3.4 Analysis of Surface Residues

4.0 Phase 4: Evaluation 2
- 4.1 Short Loop Devices - Yield and Reliability
- 4.2 Cost of Ownership Analysis (Water, Energy, Throughput, Yield)

Appendix III:

ELECTRODEIONIZATION EVALUATION IN A SEMICONDUCTOR FAB RECYCLE SYSTEM

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Abstract

Recycling of water in semiconductor fabs has become an attractive option for meeting the aggressive goals of the SIA's *Roadmap*[1] for reduced water consumption and waste stream discharge. However, the recommended system configuration for recycling more than 50% of fab rinse water usually includes pretreatment of recovered water, with Ion Exchange (IX) beds, to bring it to reverse osmosis (RO) product grade. Alternately, recovered water can be returned to the ultrapure water (UPW) generation stream at a pre-RO point, but this involves an upsized RO system, the possible introduction of high levels of sulfate (a problem with feed water with calcium present), increased cost of ownership (COO), and rejection of up to 40 % of the water recovered.

A technology that utilizes an electric current and ion exchange resins, and needs no chemical regenerations, electrodeionization (EDI) has been used in place of primary loop IX resins for many years. Its properties in this application are well known, and articles continue to be published touting its merits.[2]

The perception that fab rinse water properties are not well known and fluctuating has kept EDI from being more than a curiosity in recycle engineering. However, knowledge about

recovered water has recently increased significantly through projects with International Sematech and Sandia National Laboratory. Contrary to current opinion, the appropriate EDI unit could allow water recovery well into the 90 % range with little effort, and bring with it a concomitant reduction in water usage and discharge, and an impressive COO reduction. This paper presents the results of an EDI installation into a water system that had already been recycling, using classical IX resins. New water recovery percentages and economic figures show the merits of the application of this technology.

Introduction

For years, water conservation efforts in the Semiconductor Industry have been focused on using the inevitable wastewater from ultrafiltration, reverse osmosis, and fab rinse processes, to feed scrubbers, chillers, and horticultural efforts. Recently, fabs are recycling (returning to the fab, not just reusing) much more water because of its strongly positive impact on COO. Recycling has the effect of lowering contamination levels in polish loops, and it has helped achieve success in meeting feed and discharge limitations imposed by environmental concerns (such as in the San Jose Bay area).

Surprisingly, the decision to recycle has been a difficult one. Comparisons of the positive results of conservation efforts to the negatives of not conserving have lacked good quantitative data. Too frequently, proposed conservation programs are victims of management decisions based on outdated or incomplete accounting models. DI and Process Engineers trying to promote projects that incorporate process improvements and environmental awareness are frustrated by the cumbersome project cost justification required to move forward. Incontrovertible results with an amazing return on the investment are needed for quick approval.

Heretofore, methods of water conservation promising and delivering more impressive results have been limited to a few options, and all on the 'upstream' end (reducing point of use water consumption). One such method is in elimination of strong chemicals needing extended rinsing (e.g., ozonated UPW replacing sulfuric acid for cleaning and stripping photoresist). Also, some tools using spray technology for chemical and rinse processing are particularly successful. Another method being implemented in fabs with current immersion tank-style wetbench equipment is Rinse Optimization. Finally, at least one equipment manufacturer has embodied the principles of *Extreme Rinse Optimization*[3]. Reductions of water use approaching 90 % are attainable with the right rinse implementation.

Projects with strong financial advantages, when coupled with conservation efforts (for example, instituting a program in an existing facility, Design for Environment, or recycling), need disruptive technology to spearhead a new paradigm. This technology must have the hope of bringing radically new levels of performance to either a retrofit or a new design. When this paradigm matures, the decision to recycle would be as obvious as, for example, the decision to include reverse osmosis in a UPW train has been. It's conceivable that EDI in a recycle system can create just such a new philosophy.

Presented here is the 'downstream' end (at the drain) technology that fully complements, not replaces, all of the above methods of water use reduction. This work summarizes initial efforts to characterize EDI as an efficient, robust, and cost-effective means to either retrofit or install a new recycle system. A unit was installed in parallel with existing cation-anion exchange resin beds to compare results with only those components as significant variables. The challenge in this work is to drive rinse water recovery from tank process wet benches to an extreme. The Summary section will include a comparison of the COO from recycling with EDI to that of no recycling.

Experimental Results

A. Selection

EDI equipment has not been targeted for recycling water. The technology has invariably been specified for performance in a primary water loop application. Research and applications of EDI have been primarily, and possibly exclusively, on water generation, versus water recovery. For example, in ULTRAPURE WATER Europe '98, held in 9/98, the EDI papers dealt with lowering conductivity for on-line instrumentation needs, and generation of DI water, with a focus on carbonic, silicic and other weak acids. Marketing literature from the several EDI vendors typically includes claims on how EDI handles boron, silica, CFU bacteria, TOC and CO2, and advances in achieving 18 megohm-cm (ultrapure) quality. Potential EDI customers are cited papers about replacement of primary IX beds; CO2, silica and other ion removal kinetics; COO of IX bed replacement[2] and applications in power generation (boiler feed). Feedwater, universally RO product, is almost always at a conductivity of less than 5-6 uS/cm.

We first required that the unit accept feedwater conductivities of up to **250 uS/cm**, a value we considered sufficient to allow over 95% recycle. Monitoring at our site and others indicated that this level would represent the average high conductivity value resulting from moderate chemical processing. There would be enough dilution of rinse chemistries with trickle flows to keep the average conductivity of collected rinse waters at this relatively low level. Diversion of the first few quick-dumps from selected wet benches could also assist in keeping conductivity below an EDI's upper limit. With some extra capacity in the EDI, recycling of its product water to mix with the feed would also help during an occasional, particularly conductive event.

Coupled with this very high feed conductance tolerance, fortunately, was the much less stringent requirement that we needed EDI product water to only be better than RO product water. We set a **product conductivity target of one uS/cm** (1 megohm-cm) or better, versus fifteen megohm-cm, of which EDI is capable in a typical primary bed application. This value, though low, would prevent an increase of regenerations needed on the existing primary mixed beds--a poor trade-off for the elimination of regenerations in the recycle system.

A third requirement of the EDI was that it tolerates **high concentrations of sulfuric acid** and some **fluorides**. There are a few benches with strong fluoride mixtures. Most of the contamination in our collected rinse water is from SPM (sulfuric acid-hydrogen peroxide mixture) processing. When rejected to an EDI waste stream, it could reach quite low pH values (consider a 250 uS/cm stream of sulfuric acid increased by a factor of twenty in an EDI's concentrate stream).

The fourth requirement dealt with the volume of water to be handled. The unit had to have a **recovery rate greater than 90 %; output capability of 100 gpm.** A high recovery rate was needed to give us an overall recycle yield of greater than 90 %. The capacity of 100 gpm would allow us to start recycling water from other sources on our site, and cover an increase in fab operations.

Fears were expressed from several EDI vendors. Not only were we asking for performance at a high feed conductivity, but also it was recycled water at that: perceived as containing unknown quantities of unknown chemicals, with large swings in concentration. Here's what they said, and our justification to feel optimistic:

Issue:	***vendors Consensus:***	***Recycle view:***
Feed stream contents	Conductivity too high	To Be Determined (TBD)
	Conductivity too variable	Variable, but 'too' is subjective. TBD
	Unknown components	Known components-unlike city water.
Concentrate stream conductivity	Too high--will deposit scale	Won't scale--no cations except ammonium ion, unlike city water.
	pH too low	TBD
Organics	Too many	Virtually none, unlike city water.
Iron contamination	EDI very sensitive	No Iron in our fab water!
Hydrogen Peroxide	Sensitive--must avoid	Removed in Carbon Bed.
COO	Should be OK	Should be impressive!

Table 1. Gap analysis: EDI vendors commented on the requirements for EDI when used as a replacement for primary resin beds. Compare that to the use of EDI in a recycle system.

After several interesting but unsuccessful discussions with other vendors, we were fortunate to find that our needs could be met with a unit manufactured by Ionics, Incorporated, of Watertown, MA. Although they had considerable experience with EDI applications in primary loops, they were now entering a regime in which they had none.

The correct size for our water system happened to be their smallest, the EDI 50, a 50 gpm product stream unit. The EDI 50 has a stated recovery of 95%, with a few gpm carrying concentrated reject ions to waste. Below is a table showing the feedwater characteristics for this EDI as intended to be used in a primary loop application, and an estimate of our actual feedwater characteristics. A good description of the basic requirements in a primary loop application can be found in the reference to Ionics' web site[4]. The feedwater conductivity in recycle operation could be controlled somewhat by varying the fraction of rinse water recovered from the wet benches, since contamination is a strong function of the delay time from the start of rinsing.

Parameter	***Typical Feedwater Characteristics--Classic EDI***	***--Needs as Used in Recycle***
Conductivity	< 40 uS/cm	<300 uS/cm
Hardness	<0.25-1.0 ppm as CaCO3	No 'hardness' cations
TOC	<0.5 ppm	<100 ppb
Pressure	20-50 psi.	Dial-in
Temperature	10 to 35^{o} C	Keep it <30^{o} C
pH	4 to 10	Tolerate <2
Chlorine	<0.1 ppm	None
Fe, Mn, Sulfide	<0.01 ppm	None
CO2	<10 ppm	Highly variable, generally low

Table 2. Feedwater requirements as stated by EDI vendors compared to characteristics of the water collected for recycling.

Note that in this application, the specification for input conductivity was required to be low for the product water to meet that of a mixed primary bed IX. Since we wanted only to meet or exceed the quality of water at the point of injection to the RO product tank, we asked for only 1 uS/cm for an output specification.

Also of concern was the reject stream make-up. Our original desire was to provide the water for this from other sources, perhaps UF or RO reject, so as to maximize overall rinse water recovery. However, our other sources generally derive from untreated city water, with typical hardness cations. As we expected to discharge sulfate-containing water, which would likely cause frequent episodes of scaling, the collected rinse water was used instead.

B. Installation

The EDI unit was installed in a temporary location next to the existing recycle line. The connections to the line are shown in Figure 1. If needed, the original IX resins could be manually selected to treat the water, or even both the EDI and IX could be used for added capacity.

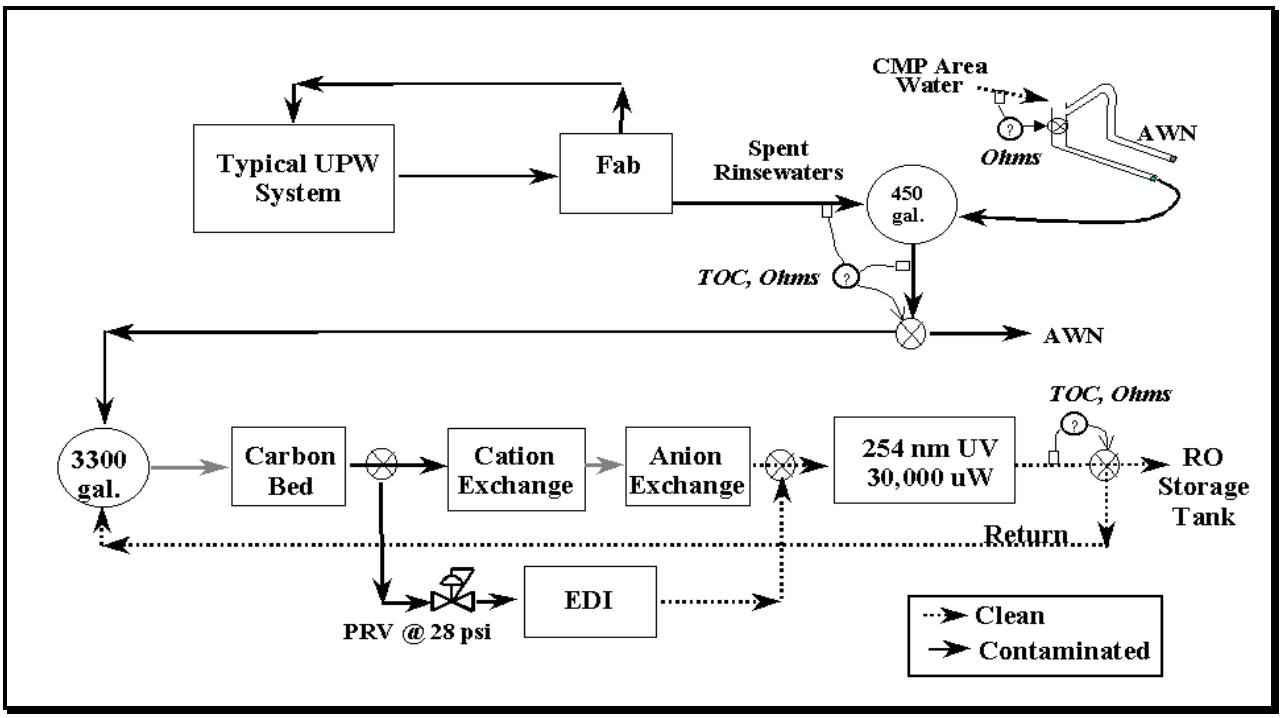

Figure 1. Plumbing of the EDI in parallel with existing IX resins. Feed pressure was dropped to meet EDI specifications. Italics are measurement points; values exceeding limits force water to AWN.

The interface to the EDI was fairly straightforward. The existing recycle system pump provided almost twice the pressure needed for the stack to operate, so a regulator was added.

Figure 2 shows an overview of the plumbing internal to the EDI, supplied by the vendor. It generally illustrates a product path, a concentrated reject stream path, and electrical power for the stack. . The output pressure from the EDI was adequate to deliver the water to the RO storage tank. A check valve was also installed in the product line in an attempt to minimize changes in product line resistance that would be reflected back through to the stack output.

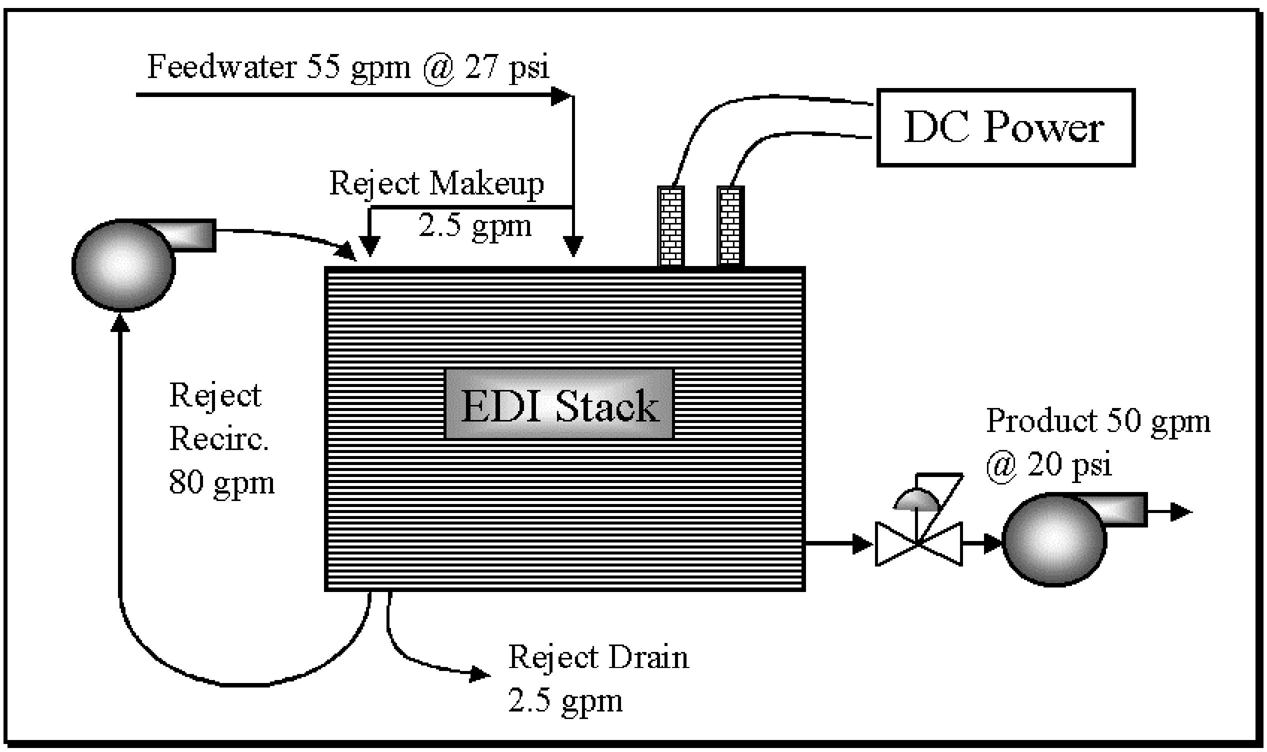

Figure 2. EDI plumbing supplied by the vendor. A constant pressure drop across the stack must be maintained with concentrate recirculation and feed/product streams.

C. Startup and Running

At initial startup, the input pressure was adjusted to provide about 55-gpm flow. Simultaneously, the concentrate stream recirculation flow was adjusted to set the input side pressure to a few pounds less than the product feed pressure. To avoid an extreme pressure difference in the event of an EDI shutdown, the feed pump in the existing recycle system was wired to the EMO of the EDI. If the EDI shut down, all water flow would be stopped.

Data were recorded about three times daily, except for special events. Figure 3 is a chart of some of the recorded values obtained from monitoring the unit's various parameters. The scale on the left is logarithmic to cover the ranges of the three important variables. Feed conductivity (diamonds) ranged from a low of 3 to a high of 1500 uS/cm. Product resistivity (squares) is in kiloohm-cm; the highest value reached is almost 18000 kiloohm-cm, or 18 megohm-cm. Stack power (X's) is in kilowatts.

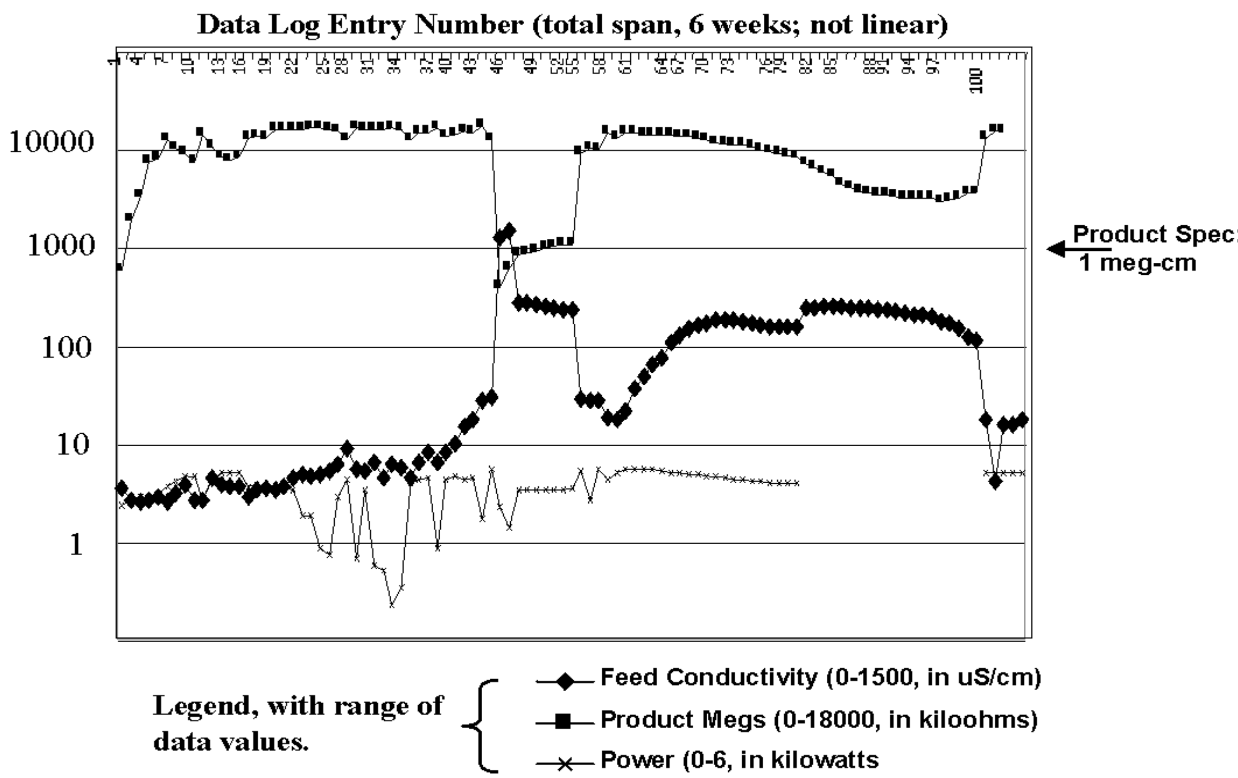

Figure 3. Data Log Chart (DLC) of EDI performance over two weeks. Our feed conductivity spec was chosen to be that which produced one megohm-cm water. Power is calculated from DC volt- and amp-meters. It includes only stack power dissipation.

Operating data were taken right from the initial turn-on. The first 14 points on the Data Log Chart (DLC) were roughly 1/2 hour apart. Within a very few minutes, product water resistivity was approaching one megohm-cm, initially low due to the ion loading of the as-purchased stack resin. Over several hours, the ions in the new stack were removed by the current flow. By the next day, we were seeing values of resistivity over 17 megohm-cm.

For several days (DLC points 15-35), feed water conductivity was running in the 2-10 uS/cm range, unusually low even for our low-use fab. Because of the extra capacity of the EDI at 50 gpm, occasional recirculation of the product to the collection tank contributed to the low feed conductivities. During this time, the balance of internal chemistries shifted, causing a marked decrease in the amperage through the stack. Since it normally operates in a 'constant voltage' mode, the stack consumed much less power during these intervals, averaging about 2 kilowatts. Typically, about six kilowatts were consumed for the rest of the range of feed conductivities.

Feedwater conductivity remained low, so we had the good fortune of being able to increase it under control to test the EDI. The first trials required two system changes. First, at the 450-gallon collection tank (see Figure 1), the diversion criteria based on conductivity was removed. That is, all water was acceptable (based on conductivity). Second, the remainder of wetbenches in our fab were connected to the recycle system. These benches had known process chemistry leaks to the water collection drain. If plumbed to the recycle system before EDI, unacceptable levels of contamination would have elicited much too frequent IX regenerations.

Conductivity at the first collection tank increased to a fairly consistent 60 uS/cm for a few days. The feed conductivity to the EDI, because of the recirculation around the recycle system to absorb the extra capacity of the EDI, settled in at around 30 uS/cm. The data during this time (DLC points 40-43) showed a slight drop in product resistivity, averaging around 15 megohm-cm. Power consumed during this period may have fluctuated due to changing chemistries within the stack prior to taking data readings, which will be discussed in the Summary section.

Finally, to stress the EDI to the maximum feed conductivity the vendor estimated to be the EDI's capability, chemistry was administered to the system. For over an hour, at about five-minute intervals, about 200 milliliters of sulfuric-peroxide mix, buffered etch chemistry, 5% HF, phosphoric acid, and/or RCA chemistry were dumped into drains scattered around the fab. All of this water was collected in the 450-gallon tank, pumped to the 3300-gallon tank, and sent through the EDI.

The event is shown in Figure 3., DLC points 43-54. The conductivity in the 450-gallon tank was above 10,000 uS/cm at times, a level we did not intentionally wish to create. Feed to the EDI reached about 1500 uS/cm, about six times the conductivity we expected as a maximum feed value. The product resistivity at the maximum was still over one megohm-cm, but after another hour, the ionic load in the stack, or in the concentrate stream, drove the output conductivity up to just under 2 uS/cm. Shortly, the feed conductivity improved to just under 300 uS/cm (DLC point 45). For the next six points, as the feed conductivity swept through 260 uS/cm over about 45 minutes, product resistivity rose above 1 megohm-cm, just as the vendor had stated. The data after that event show a gradual increase in resistivity to levels prior to the over-stress test.

Another experiment, between points 57 and 93, shows that as the feed conductivity increases, product resistivity decreases, but with some lag. For example, the first jump in feed conductivity at points 57-65 shows the product resistivity barely dropping. When the feed is held at about 150 uS for points 69-77, the product resistivity continues to drop. Then at point 79, the feed was abruptly increased and held steady. However, product resistivity still dropped through the range of points 80 to 95, even towards the end where feed decreased to 110 uS. This behavior will be explained below.

Discussion

A. Technology

The EDI unit was able to meet our specifications in terms of treating high levels of conductivity, as anticipated. Its response can be categorized broadly as follows:

- At low levels of feed conductivity (0-6 uS/cm), the unit drew relatively small amounts of current and produced water of 13-17 megohm-cm resistivity. It behaved this way for days, with the stack consuming less than a kilowatt. It was probably due to the low concentration of rejected ions in the concentrate stream. This condition was new to the vendor of the EDI, but there were no apparent deleterious effects. Early in the experiments it was felt that the higher megohm-cm range of product would be reached if the concentrate stream had higher conductivity, effecting a more complete removal of ions with higher currents. This theory was shown to be just opposite of the evidence, as is shown below.

- At moderate levels of feed conductivity (6-50 uS/cm), the unit still produces high resistivity water (>10 megohm-cm consistently), but draws more amperage from its power supply. This is actually normal operation. In a primary loop application, the vendor supplies a salt injection tank and pump to optionally add ions to the concentrate stream. We chose not to introduce more ions, but instead tried throttling the reject stream flow down to maintain an ionic level optimum for operation. This is not the normal mode of operation, but if pressure deltas are kept in the right direction and magnitude, this method could reduce water discharge and reduce the complexity of operation and use of chemicals. However, as shown in a Figure 5, system performance indicated we did *not* want higher conductivities in the concentrate stream.

- At high levels of feed conductivity (60-300 uS/cm), the EDI draws maximum current. Product resistivity stays relatively high even with an increased load to the system, falling between the two curves shown in Figure 4. The power supply to the stack showed signs of reaching its maximum capacity at the high end of this range, as both voltage and current drop.

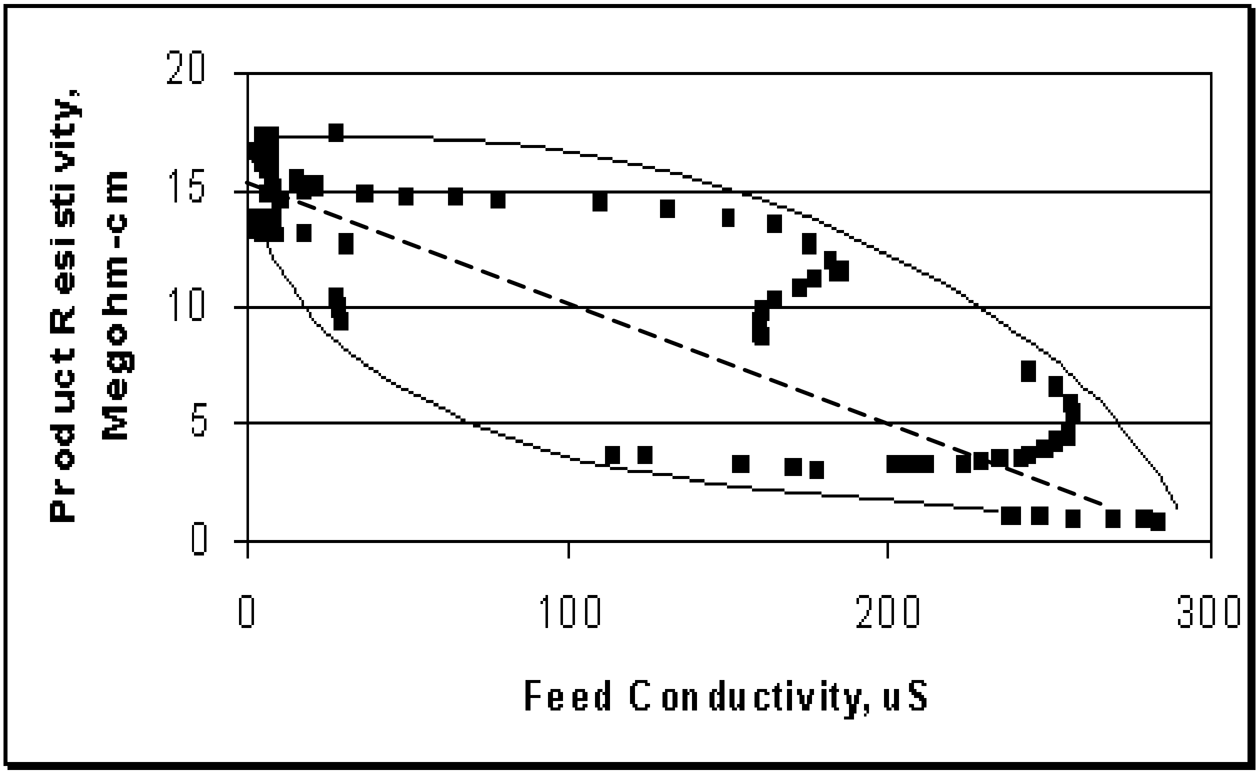

Figure 4. Product water resistivity in megohm-cm versus feed conductivity in uS/cm. The upper curve bounds the product resistivity when the feed conductivity is increasing (arrow to right); the lower curve, when it is decreasing (arrow to left). The dashed line approximates the equilibrium product resistivity achieved only after several hours of constant conductivity feed water. The lag in response between feed water conductivity and product water resistivity accounts for the large area between the two solid curves.

- With an abnormally high conductivity event (>300 uS), the EDI performed very well (the two data above 1.4 milliSiemen/cm) are not plotted on Figure 4 to keep the other data easier to read). It's postulated that the resins in the stack load with ions during an extended impulse of conductivity, but the stack current cannot sweep the ions out fast enough. If of short enough duration, the event will be removed by the stack current before product water resistivity becomes too poor to use. With a longer duration feed event, the ionic loading exceeds the capability of the stack resins and/or power supply. Stack voltage drops, and the water resistivity degrades. When the event passes, the stack recovers fairly quickly (minutes) and resistivity improves.

- When the feed conductivity increases rapidly from a low level, the product resistivity predictably drops, but still stays high. The concentrate stream builds up ions, and will soon be at the ionic strength determined by feed/reject stream flow ratios. This response, product resistivity staying high out of proportion to the reject ratios, is a result of the concentrate stream conductivity being lower than the reject ratios predict until equilibrium is reached. As conductivity of the concentrate stream rises, the resistivity of the product falls, even if the feed conductivity held constant. This can be seen in Figure 4 at 165 uS, where the feed conductivity was held between 155 and 165 for an hour, during which time the product resistivity dropped from 12 megohm-cm to just over 8. During this time, the concentrate conductivity rose from about 600 uS/cm to 1200 uS/cm, which *fully* accounted for the product resistivity change (see below, Figure 5 and explanation).

- Conversely, when the feed conductivity drops from an elevated level, response by the product stream is somewhat lagging. Even though the concentrate stream is fully charged with conductive ions, and the unit can pass current at its maximum, the high ionic levels in the concentrate stream effect product resistivity more than the feed conductivity. The product resistivity will stay lower than the equilibrium value, generally following the lower curve in Figure 4, as feed conductivity decreases from right to left.

Figure 5 shows the strong correlation between *concentrate stream* conductivity and product resistivity. Product resistivity is related to *feed* conductivity only after equilibrium (after hours of constant feed conductivity). The figure shows that the product water resistivity and concentrate stream conductivity data fit a (six-degree polynomial) trend line extremely well.

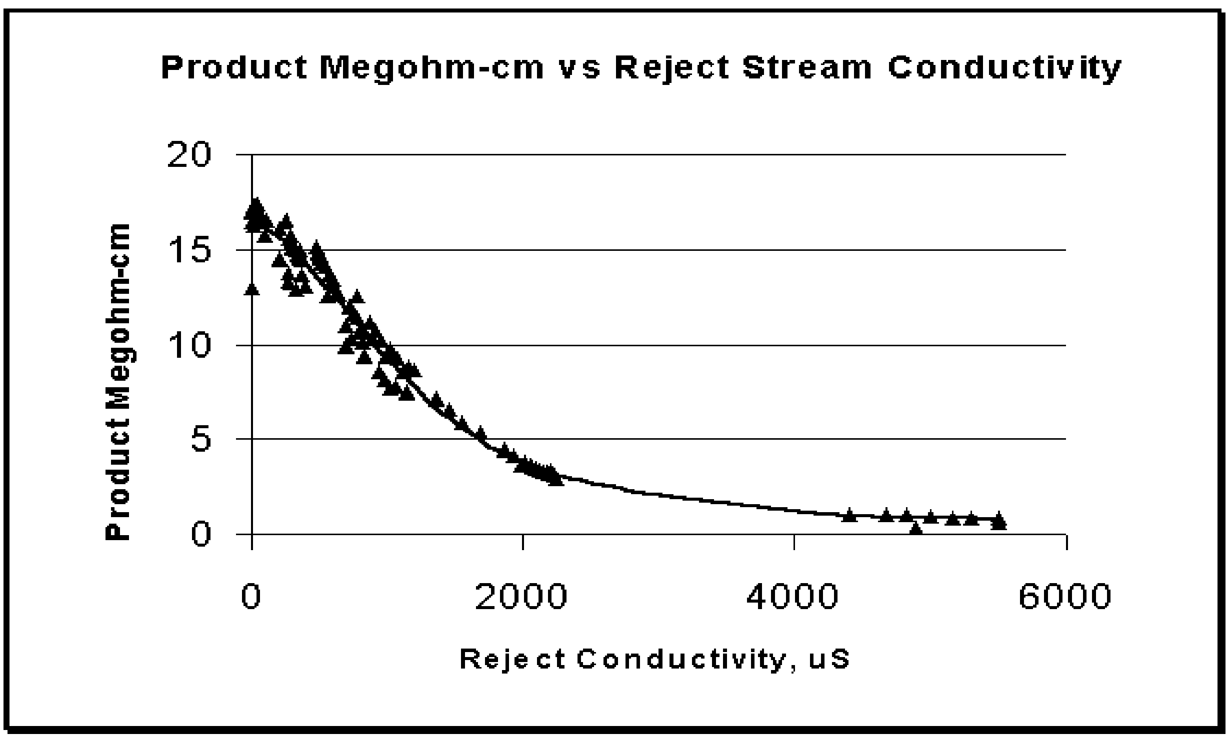

Figure 5. Relationship between product resistivity and concentrate stream conductivity. The excellent fit to the trend line (R^2=0.975) indicates a direct relationship between concentrate and product ionic strength. A simple exponential curve (R^2=.91) is also close.

The relationship between product resistivity and feed water conductivity has already been shown to be very dependent on the direction of the feed conductivity change (Figure 3). The curve in Figure 5, however, can be used to predict product water resistivity independent of the direction of change, or even magnitude, of the feed water conductivity.   This unexpected result is likely explained by the physical arrangement of resins, flow paths, and differential pressures between paths. Further, the ions contributing to this lowered product resistivity are from dissociated sulfuric acid, which is strongly conductive, and not easily discriminated by ion selective membranes. More typically, mixtures of chemistries from a balanced semiconductor fab will have lower specific conductivities and higher membrane rejection, thereby producing higher product resistivities.

The non-linear characteristics described above do not effect the desired result of obtaining high resistivity water for recycling. These results may offer some insight for vendors of EDI equipment to enhance the design for operation in a recycle application.

Samples of feed, product and reject streams have shown only the constituents of rinse water from wafer processing. Thus far, no elements that would indicate dissolution of the materials of construction of the EDI unit have been detected at elevated levels. TOC amounts tracked during events of high feed water conductivity and at steady state have shown at most a few ppb elevation. Even this may not be attributable to the EDI itself. Silica and Boron rejection will be investigated soon.

B. Estimate of Economic Benefits

The following is an estimate of the some of the costs of operation of the relevant generation and recycling areas of our DI system. Some of the benefits are immediate; others are delayed (like depreciation, which is not included), or very site-dependent (like labor arrangements, not included).

The biggest outlay, of course, was the EDI unit itself. As a direct replacement for IX beds in place at our site, minimum plumbing changes were needed. The installed cost was somewhat under $100,000 for the 50-gpm capacity unit we purchased.

1. The reduced operating time of the RO would allow that $7200 per year for pre-RO filters would be avoided.

2. Elimination of the recycle IX beds and processing of higher resistivity water from the EDI would result in savings of $5200 for regeneration chemicals for the Recycle System resins, and $1000 per year for Primaries.

3. The reduced operating time of the RO would allow that $2000 per year for membrane cleaners would be avoided.

4. Electric charges for a 25 BHP pump are about $3100/year (at $0.042/kwh, using faceplate consumption values). Running at 100% of capacity (typical for a system with no recycle), the cost of electricity for the various pumps, is:

a. Ultrafilter pump (booster): 15 BHP=>$1800 per year;
b. RO pumps: 25 BHP x2 => $6200 per year.

Because these pumps don't operate when recycled water is used, electricity charge savings proportional to the percentage recycle are obtained. If they ran at 10 % duty cycle, yearly charges would be cut to $800 from $8000.

On the negative side, the EDI installation would need three 7.5 BHP pumps. They would consume about 7.4 kilowatts/hour, or 144 kWh/day. At $.042/kWh, this yields about $7.45/day, or $2723/year.

5. Last, the raw water supply and discharge costs are substantial. In our system, recycling 45 Kgpd reduces discharge by about 80 Kgpd, due to inefficiencies in the UPW front end. The cost for this ($4.64/Kgal for supply and discharge fees, Palo Alto) results in a savings of $4.64 X 80, or $387/day savings. This sums to $141,000 per year.

Item:	***Cost without EDI***	***Cost with EDI***	***UPW Operation Savings***
Electric Power	$6,200 + $1,800	$800 + $2723	$4,377
Chemicals (regen, cleaning)	$8,000	$800	$6,200
Pre-RO Filters	$8,000	$800	$7,200
Cost of water/discharge	$156,666	$15,666	$141,000
Misc. items (maintenance)	$3,000	$3,000	0
M&L to install 50 GPM EDI		$100,000	-$100,000
Totals*	$183,666	$123,789	**$59,877**
*Totals*** with M&L upgrade to 100 gpm	$367,332 (twice the 50 gpm costs)	$50,000 + $123,789	**$193,543**

Table 3. Summary of COO savings when Recycling with EDI. The totals shown are with and without a one-time saving of $60,000, as explained above.

Table 3 shows a summary of the savings estimates. The Totals* include materials, labor, and net gain for a 50-gpm installation; Totals** shows this for a 100-gpm installation. The 100-gpm figure assumes the original UPW operation needed twice the pumping, chemicals, etc. of the 50-gpm system. In summary, the first year savings from an EDI installation at the 50 gpm rate would be $60K; in subsequent years, $160K. For a 100-gpm unit, first year savings would be $194K, and subsequent years would be $344K.

Summary

We can fill in some of the TBD's from Table 1 now. The feedwater conductivity can be elevated and variable, and the EDI will still produce high resistivity water for injection into the main UPW system at the RO product tank. There's no evidence of scaling or other chemistry-related performance degradation. The pH is being monitored by sampling the reject stream during high conductivity events; no problems so far. Testing for metal contamination (the EDI electrodes slowly dissolving?) is ongoing. Hydrogen peroxide has not been detected. Finally, the brief look at economics has shown a very positive result. There has been no maintenance required, no regenerations, and it operates with strong or weak feed streams with no technician involvement.

Electrodeionization has proven to be of significant value as a recycle system component. In our installation it is currently treating an estimated 90% of the collected water, including every rinse from most (including SPM) process baths. The remainder will come on line as the recycle programming in some benches is changed. The loss due to the reject stream from the EDI brings recovery to about 86%. We'll be looking into reject control to lower water discharge, and also gain understanding of the relationship between product resistivity and concentrate stream conductivity. Alternatives will be sought to match the size of the unit with the recovered water flow, to minimize local recycling of EDI product water and increase recovery.

In the future, TOC, silica and boron will be the focus of continued testing. We will also optimize operating parameters to lower the interaction causing product resistivity to be so strongly related to concentrate stream conductivity. We anticipate developing other uses for DI from EDI water that may, like recycling, have been assumed inappropriate--for example, in near-zero blowdown cooling towers and closed-loop scrubbing operations. This technology has made available numerous opportunities for water reuse heretofore felt prohibitive due to cost or unknown water quality.

Acknowledgements

This work was made possible by the generous donation of unending engineering support from Ionics, Incorporated, of Watertown, MA. Not that the unit malfunctioned in any way: they responded to my strange requests and potential threats to the EDI unit with professionalism and much patience.

Biography

Russ Parker, Ph.D.

Dr. Parker is a member of the ULSI Research Laboratory at Hewlett Packard Laboratories in Palo Alto, CA. He is a member of the Sematech S116 Water Use Optimization/Conservation project, and is involved in various research projects with the ERC[5], Stanford University, and Sematech. Dr. Parker has a Ph.D. in Analytical Chemistry from Purdue University.

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[5] NSF/ERC information at http://www.erc.arizona.edu/

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